Naval Research Laboratory

Washington, DC 20375-5320



NRL/MR/6110--06-9006

Gas Hydrate Exploration, Mid Chilean Coast; Geochemical-Geophysical Survey

RICHARD B. COFFIN

Chemical Dynamics and Diagnostics Branch Chemistry Division

Juan Diaz

Pontificia Universidad Católica de Valparaíso Valparaíso, Chile

JOAN GARDNER

Marine Physics Branch Marine Geosciences Division

JAVIER SELLANES

Linivargity of Cor

University of Concepción Concepción, Chile

December 27, 2006

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)	
27-12-2006	Memorandum Report	Cruise Report-Mid Chilean Margin October 2004	
4. TITLE AND SUBTITLE		5a. CONTRACT NUMBER	
Gas Hydrate Exploration, Mid Chilea	n Coast; Geochemical-Geophysical Survey	5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
Richard B. Coffin, Juan Diaz,* Joan C	Gardner, and Javier Sellanes†	5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAM	ME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER	
Naval Research Laboratory			
4555 Overlook Avenue, SW Washington, DC 20375-5320		NRL/MR/611006-9006	
9. SPONSORING / MONITORING AGEN	NCY NAME(S) AND ADDRESS(ES)	10. SPONSOR / MONITOR'S ACRONYM(S)	
Office of Naval Research Global (ON	RG)		
One Liberty Center (Suite 1426)			
875 North Randolph Street		11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
Arlington, VA 22203-1995		NOWIDEN(S)	
12. DISTRIBUTION / AVAILABILITY ST	ATEMENT		
Approved for public release; distribut	ion is unlimited.		
13. SUPPLEMENTARY NOTES			

13. SUPPLEMENTARY NOTES

*Pontificia Universidad Católica de Valparaíso †University of Concepción Valparaíso, Chile Concepción, Chile

14. ABSTRACT

The Naval Research Laboratory (NRL), supported through ONRG-Chile, DOE/NETL, and ONR, participated in a research cruise along the mid Chilean coast. Specific research topics addressed by NRL in this program include survey and prediction of geotechnical and geoacoustical anomalies, estimation of coastal hydrate distribution, refining protocol for hydrate exploration, and understanding the variation in microbial community diversity in hydrate-rich regions. The Chile-FONDEF goal in this program is to locate hydrates along the Chilean coast in terms of distribution and methane content for understanding the available energy and geological hazards. This effort integrates future energy exploration with ocean and climate research topics. The examination of sediments in this region was conducted in a collaborative effort between NRL, Milbar Hydrotest, Inc., Virginia Institute of Marine Science, Pontificia Universidad Católica de Valparaíso, University of Concepción, and Rice University. Piston coring, heatflow and biological sample sites were selected in two regions on the basis of previous seismic surveys taken during April 2003 and work conducted by scientists at the University of Concepción. The coring and heatflow, along the previous NRL seismic line (DTAGS), was run between 36'10.38S, 73'35.72W and 36'12.50S, 73'3976W. Sulfate, sulfide, methane, chloride, and dissolved inorganic carbon (DIC) profiles from piston core porewater samples, heatflow data and seismic profiles were combined to survey the presence of hydrates in this region. Fourteen out of 15 piston cores in this region were successful. Heatflow data was collected at 21 sites through the transect. An additional sample region was selected at the base of a 40 meter sub-sea mound located at 36'22S, 73'43W where biologists from University of Concepción located large concentrations of benthic organisms. Two piston cores were collected in this region. Attempts for obtaining heatflow in this region were not successful due to probes being bent or shredded upon delivery into the sediment.

Another objective during this cruise was the integration of geochemical data with the biological communities over the regions of sediments that contained methane hydrates. Recent benthic surveys in the bathyal area off Concepción revealed important clues indicating the existence of methane seepage and related biological chemosynthetic communities. Shell fragments of two species of bivalves of the genus Calyptogena (VESICOMYIDAE) and one species of Acharax (SOLEMYIDAE) were retrieved in two dredge hauls off Concepción (36°21.46'S, 73°44.08'W, water depth 934 m, and 36°16.40'S, 73°40.70', 651 m). An important quantity of carbonate crusts were also collected, indicating that anaerobic oxidation of methane is occurring. The accompanying non-obligate chemosynthetic fauna from one of the hauls was very diverse, containing several species apparently not before observed. The geochemical data collected from this region found shallow profiles for methane and sulfate. Hydrate samples were obtained through one of the cores at the base of this mound. On board hydrate gas analysis resulted in a conclusion that the hydrates are from biogenic origin.

Methane hydrate; Exploration; Geochemistry; Seismic; Heatflow

16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Richard B. Coffin	
a. REPORT	b. ABSTRACT	c. THIS PAGE	UL	63	19b. TELEPHONE NUMBER (include area
Unclassified	Unclassified	Unclassified			(202) 767-0065

Cruise Report – Mid Chilean Margin, October 2004

Gas Hydrate Exploration, Mid Chilean Coast; Geochemical-Geophysical Survey

LEAD SCIENTISTS:

Richard B. Coffin, NRL-DC

Juan Diaz, Pontificia Universidad Catolica de Valparaiso

Joan Gardner, NRL-DC

Javier Sellanes, University of Concepción

POC:

Richard B. Coffin, Ph. D. Section Head, Code 6114 Marine Biogeochemistry Section Naval Research Laboratory 4555 Overlook Avenue, SW Washington, DC 20375 email - rcoffin@ccs.nrl.navy.mil













Sponsors: ONRG International Methane Hydrate Research and Development, ONR, Department of Energy NETL

ii. DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability of responsibility for the accuracy, completeness, or usefulness of any information, apparatus product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

iii. TABLE OF CONTENTS

i.	Title Page	1
ii.	Disclaimer	2
iii.	Table of Contents	3
iv.	Table of Figures	4
v.	Table of Tables	5
vi.	Table of Appendices	5
vii.	Abstract	6
I.	Introduction	8
II.	Hydrate Exploration Team	9
III.	Objectives	10
IV.	Site Description	11
V.	Parameters	15
VI.	Equipment and Instruments on Board	15
VII.	Methods	20
VIII.	Preliminary Results	25
IX.	Preliminary Conclusions	35
X.	Future Goals	36
XI.	References	37
XII.	Daily Activity	38

iv. TABLE OF FIGURES

Figure 1: Sample region along the mid Chilean coast	11
Figure 2: Piston core and heatflow site selection along the April 2003 DTAGS line	12
Figure 3: April 2003 DTAGS profile of mid Chilean coast used for selection of piston core and heatflow sample locations	12
Figure 4: Sampling mound topography with sediment Agassiz trawl sample lines and piston core site selections	13
Figure 5: MILBAR Hydrotest, Inc. designed a new piston core that was tested for geochemical sampling during this cruise. The new design for the piston core provided a more safe core delivery and retrieval protocol with changes in the messenger weight and triggering mechanism.	16
Figure 6: Cores sleeves were taken from the piston core system and prepared for the porewater press, onboard analysis and sample storage on the deck with care not to contaminate samples that will be analyzed for natural radiocarbon isotope analysis	17
Figure 7: On board analytical instruments used for measuring core porewater methane, sulfate, chloride, sulfide and dissolved inorganic carbon concentrations	17
Figure 8: NRL's telemetering marine heat-flow probe system, designed and built by the Geological Survey of Canada, is designed to measure temperature gradients and in-situ thermal conductivity of sediments	18
Figure 9: The Agassiz trawl was used for sample biological abundance and diversity in region along the Chilean shelf that were thought to be rich in methane hydrates providing energy through microbial cycling at the base of the food chain.	19
Figure 10: A water sampling rosette equipped with a depth finder, CTD probes and 24 1-L Niskin bottles was used to sample the water column for methane transported from the sediments.	20
Figure 11: A comparison of core sulfate, methane, sulfide, dissolved inorganic carbon and chloride porewater samples taken along the previous DTAGS line. Core 11 was taken over a BSR wipe out region and Core 10 was taken over a BSR	27
Figure 12: Porewater profiles for sulfate, methane, sulfide, dissolved inorganic carbon and chloride concentrations from 2 cores at less active regions	29

Figure 13: Porewater profiles for sulfate, methane, sulfide, dissolved inorganic carbon and chloride concentrations from sediment cores taken at the base of a mound located in a south eastern region past the DTAGS survey line	. 29
Figure 14: A comparison of porewater sulfate data for the 15 cores taken along the mid Chilean coast during October 2004	30
Figure 15: A comparison of porewater methane data for the 15 cores taken along the mid Chilean coast during October 2004	31
Figure 16: A comparison of porewater sulfide data for the 15 cores taken along the mid Chilean coast during October 2004	31
Figure 17: A comparison of porewater chloride data for the 15 cores taken along the mid Chilean coast during October 2004	32
Figure 18: A comparison of porewater dissolved inorganic carbon data for the 15 cores taken along the mid Chilean coast during October 2004	32
Figure 19: Heatflow value variations (top panel) along DTAGS high resolution seismic line. Note the apparent upward perturbation of the BSR where the arrow identifying the BSR is pointing	33
V. TABLE OF TABLES	
Table 1: Research Team	9
Table 2: Officers and Crew of Vidal Gormaz	10
Table 3: Piston core and heatflow locations	. 13
Table 4: Agassiz trawl locations	14
Table 5: Relative composition of the mega- and macrofauna collected with the Agassiz trawl	35
VI. TABLE OF APPENDICES	
Appendix 1: Piston core water data	43
Appendix 2: Annex benthos overview	49

vii. ABSTRACT

NRL, supported through ONRG-Chile, DOE/NETL and ONR, participated in a research cruise along the mid Chilean coast. The NRL objectives were to enhance the integrated geochemical-geophysical data set for methane hydrate exploration and continue development of international collaboration on methane hydrate exploration. Specific research topics addressed by NRL in this program include survey and prediction of geotechnical and geoacoustical anomalies, estimation of coastal hydrate distribution, refining protocol for hydrate exploration and understanding the variation in microbial community diversity in hydrate rich regions. The Chile-FONDEF goal in this program is to locate hydrates along the Chilean coast in terms of distribution and methane content for understanding the available energy and geological hazards. This effort integrates future energy exploration with ocean and climate research topics. The examination of sediments in this region was conducted in a collaborative effort between, Naval Research Laboratory, Milbar Hydrotest, Inc., Virginia Institute of Marine Science, Pontificia Universidad Catolica de Valparaiso, University of Concepción and Rice University.

Piston coring, heatflow and biological sample sites were selected in two regions on the basis of previous seismic surveys taken during April 2003 and work conducted by scientists at the University of Concepción. The coring and heatflow, along the previous NRL seismic line (DTAGS), was run between 36'10.38S, 73'35.72W and 36'12.50S, 73'3976W. Sulfate, sulfide, methane, chloride, and dissolved inorganic carbon (DIC) profiles from piston core porewater samples, heatflow data and seismic profiles were combined to survey the presence of hydrates in this region. Fourteen out of 15 piston cores in this region were successful. Heatflow data was collected at 21 sites through the transect. An additional sample region was selected at the base of a 40 meter sub-sea mound located at 36'22S, 73'43W where biologists from University of Concepción located large concentrations of benthic organisms. Two piston cores were collected in this region. Attempts for obtaining heatflow in this region were not successful due to probes being bent or shredded upon delivery into the sediment. At one successful heatflow site, that was intended as a control site, a low value was obtained, and is thought to result from shallow penetration into a hydrate bed.

Along the previous DTAGS line selection of sample locations included regions with strong shallow and deep bottom simulating reflectors (BSR) and areas with gas wipe out zones. While there was generally good correlation between heatflow and geochemical data, the gas wipe out regions observed with the seismic profiles did not consistently correspond to high heatflow and shallow geochemical profiles. In the active geochemical and heatflow regions, the piston core profiles were found to have extremely shallow slopes for the methane and sulfate profiles with minimum values measured between 25 and 250 cm. Geochemical and heatflow data from the largest seismic wipe out point was found to have data similar to points with a strong BSR and at a less intense seismic wipe out the greatest value of vertical advection was observed.

Another objective during this cruise was the integration of geochemical data with the biological communities over the regions of sediments that contained methane hydrates. Recent benthic surveys in the bathyal area off Concepción revealed important clues indicating the existence of methane seepage and related biological chemosynthetic communities (Sellanes et al. 2004). Shell fragments of two species of bivalves of the genus *Calyptogena* (VESICOMYIDAE) and one species of *Acharax* (SOLEMYIDAE) were retrieved in two dredge hauls off Concepción (36°21.46'S 73°44.08'W, water depth 934 m, and 36°16.40'S, 73°40.70', 651 m). An important quantity of carbonate crusts were also collected, indicating that anaerobic oxidation of methane is occurring. The accompanying, non-obligate chemosynthetic fauna from one of the hauls was very diverse, containing several species apparently not before observed. The geochemical data collected from this region found shallow profiles for methane and sulfate. Hydrate samples were obtained through one of the cores at the base of this mound. On board hydrate gas analysis resulted in a conclusion that the hydrates are from biogenic origin.

Final data interpretation will be completed with a survey of additional parameters in the laboratory. Geochemical and biogeochemical parameters will include stable carbon and radiocarbon isotope analysis of a variety of carbon pools to address the biological cycling of methane. Microbial community diversity and analysis of low molecular weight acids will assist in this study. With regard to organisms collected in trawls at the sediment water column interface, it is expected that the species assemblages associated with cold seepage off Chile are similar in structure to others reported elsewhere, but should bear an important number of endemic species, many of them still unknown to science. Stable C and N isotopic signatures of the fauna will also be analyzed in order to determine the extent of the reliance of heterotrophic benthos in primary production derived from chemosynthesis.

I. INTRODUCTION

Gas hydrates, ice-like mixtures of hydrocarbon gas (mostly methane) and water are found within Arctic permafrost and within ocean sediments located along the margins of most landmasses within specific pressure-temperature boundaries. The discovery of this type of methane reservoir is exciting because it is estimated to contain at least 2 times the current estimates of fossil fuels. Because methane hydrates represent a potential new source of clean energy, international programs to determine the location and concentration of the hydrates within marine sediments have begun with strong financial, technical and intellectual commitments in several nations around the world. In some nations alternate energy is a key for economic development and methane hydrates are viewed to be worth the investment for exploration.

Parallel with national and world interest in methane hydrates an energy resevior, the Naval Research Laboratory (NRL) initiated a project which is designed to improve the understanding and develop models for the formation and dissociation of natural gas hydrates. The goal of this effort is to quantify the impact of these processes on the geoacoustic and geotechnical properties of marine sediments in littoral regions. Since hydrates are found worldwide along continental margins, a model is needed to predict the effect of hydrate deposits on these signatures in terms of Navy system operations. The current NRL project is designed to survey methane flux to surface sediments and the microbiological cycling in hydrate formation and dissociation. Data from this effort also addresses resource characterization, commercial availability, global carbon cycle, and sea floor stability. This broad array of research topics promotes the development of international collaborations.

With the NRL in-house methane hydrate research program underway, a collaborative effort between the University of Hawaii (Hawaii Natural Energy Institute) and NRL to form an international consortium for methane hydrate research was initiated. The high cost of fieldwork and the broad range in knowledge and technology in hydrate exploration throughout the world promotes a strong need for a collaborative international research program. Efforts in the development of this program have resulted in a five nation collaboration to investigate the presence of methane hydrates off the coasts of the US, Canada, Japan and Chile. These collaborations were formed through 4 workshops over the last 5 years; "International Workshop on Methane Hydrate Research and Development", with participation by 12 nations.

This is the second research cruise that NRL has joined for methane hydrate exploration off the mid Chilean coast. During March and April 2003 NRL joined a five nation collaboration between Chile, Canada, Japan Germany and the US to explore methane hydrates off the coast of Chile. NRL contribution to this exploration was high resolution seismic profiles collected using the Deep Towed Acoustic Geophysical System (DTAGS) and geochemical analysis of piston cores and heatflow probing along the DTAGS survey line. Poor weather conditions limited piston core on the 2003 expedition; only 6 piston cores were retrieved. The research presented in this report employs the DTAGS data set and preliminary geochemical data to select sites for heatflow probing

Manuscript approved September 15, 2006.

and piston coring. Geochemical analysis of core sediments and porewaters provide predictions of methane hydrates amounts in surface and deep sediments. Sulfur, methane and dissolved inorganic carbon profiles in cores are employed to predict hydrates forming deep in the sediment. Chloride is used to determine the presence of hydrates in the range of piston cores. A broad array of geochemical and microbiological parameters were incorporated into this data set for addressing the microbial role in cycling the chemicals that control methane oxidation and formation in the surface sediments.

Another aspect of this research cruise is the integration of geochemical data with the biological communities over the methane hydrate sediment regions. Recent benthic surveys in the bathyal area off Concepción revealed important clues indicating the existence of methane seepage and related biological chemosynthetic communities (Sellanes et al. in press). Shell fragments of two species of bivalves of the genus *Calyptogena* (VESICOMYIDAE) and one species of *Acharax* (SOLEMYIDAE) were retrieved in two dredge hauls near Concepción (36°21.46'S 73°44.08'W, water depth 934 m, and 36°16.40'S, 73°40.70', 651 m). An important quantity of carbonate cemented crusts was also collected, indicating that anaerobic oxidation of methane is occurring. The accompanying, non-obligate chemosynthetic fauna from one of the hauls was very diverse, containing several unidentified species.

II. HYDRATE EXPLORATION TEAM

Table 1: Research Team

Participant	Affiliation	Background	Role
Dr. Juan Díaz	PUCV	Geophysics	Chief Scientist
Dr. Richard Coffin	NRL	Geochemistry	Co-chief Scientist
John Pohlman	VIMS	Biogeochemistry	Core processing,
			porewater analysis
Dr. Leila Hamdan	NRL	Microbiology	Microbial community
			diversity
Dr. Shelby Walker	NRL	Geochemistry	Porewater geochemistry
Dr. Joan Gardner	NRL	Geophysics	Heatflow
Dr. Rick Hagen	NRL	Geophysics	Heatflow
Ross Downer	Milbar Hydrotest	Field Engineer	Piston coring
Latham Bryant	Milbar Hydrotest	Field Engineer	Piston coring
Dr. Javier Sellanes	UDEC	Benthic biology	Surface sediment
			biological diversity
Eduardo Quiroga	UDEC	Benthic biology	Suface sediment
			biological diversity
Ivana Novosel	Rice University	Geochemist	Ba & Ca concentrations
Jenny Maturana	PUCV	Ship Technician	Operate CTD
Eleonora Barroso	PUCV	Student	General assistance

Table 2: Officers and Crew of Vidal Gormaz *

Name	Rank	Function
Jorge Aguirre Moltedo	Commander	Commanding Officer
Cristian Diaz De Lartundo	Lieutenant Commander	Executive Officer
Julio Saavedra Quinteros	Lieutenant Señior Grade	Naval Engineer
Juan Pablo Olivares Arancibia	Lieutenant Junior Grade	Oceanography Officer
Matias Silva Bakker	Lieutenant Junior Grade	Watch Officer
Rodrigo Espinoza Martín	Lieutenant Junior Grade	Watch Officer
Rodrigo Mesa Furniss	Ensign	Watch Officer
Hector Salgado Narváez	Ensign	Watch Officer
Antonio Urbina Silva	Sergeant	Boatswain
Pedro Parra Consuegra	Sergeant	Welder
Eleodoro Jerez Palacios	Sergeant	Winch Operator
Pedro Bizama Mundaca	Corporal	Winch Operator
Manuel Higueras Molina	Corporal	Winch Operator
Christian Ortiz Delgado	Corporal	Seaman Poop Deck
Marcelo Troncoso Jara		Seaman Poop Deck
Andres Troncoso Ortiz		Seaman Poop Deck

^{*}The entire crew of the Vidal Gormaz is 38. The above listing is personnel that assisted with this scientific mission. Assistance with all scientific activities on the ship was appreciated.

III. OBJECTIVES

The following text is a list of objectives for this research cruise.

- 1. Advance international collaboration on methane hydrate exploration and research.
- 2. Integrate geochemical and geophysical parameters to determine hydrate locations off the coast of Concepción, Chile.
- 3. Expand the NRL hydrate data base to address the coastal variation in geotechnical properties and geoacoustic signatures.
- 4. Determine the hydrate gas sources, cycling and composition.
- 5. Survey biogeochemical influence on the methane hydrate cage gas saturation and stability.
- 6. To study the general thermal regime of the working areas.
- 7. To elucidate if there are indeed time lags between tectonic movements and hydrate destabilization.
- 8. To study the seasonal effect on heatflow measurement as a function of depth.
- 9. To describe megafaunal communities associated to methane seepage.
- 10. To characterize megafaunal chemosynthetic endosymbionts by molecular techniques.
- 11. To determine the role of chemosynthesis in fueling heterotrophic food webs.

IV. SITE DESCRIPTION

Researchers contributing to this methane hydrate survey departed from Valpariaso Chile on 7 October 2004, to participate in field work off the coast of Concepión (Figure 1). Initially, work was planned for the previous DTAGS line, the newly discovered

mound and Tolten Canyon. Weather and equipment difficulties resulted in a focus on the DTAGS line and some initial sampling on the mound.

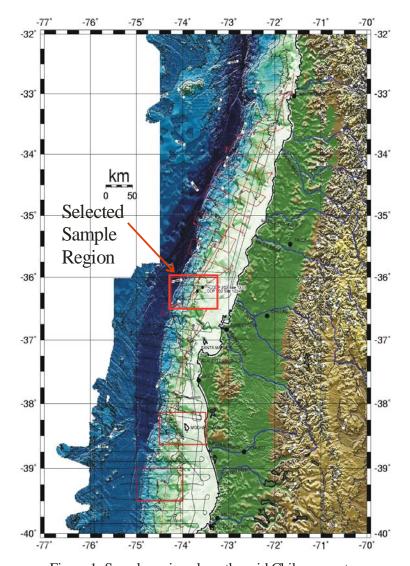


Figure 1: Sample region along the mid Chilean coast.

Coring, heatflow and biological sample sites were selected on the basis of previous seismic surveys and geochemical analysis of piston core porewaters, which took place in April 2003, and surface sediment biological sampling conducted by scientists at the University of Concepción. During April 2003, NRL conducted a DTAGS line north of Concepción running east to west in water depth ranging from 586 to 1935 m (Figure 2). This seismic profile was reviewed to determine the optimum locations for the piston coring and heatflow. Sites along the seismic profile were selected to characterize the extent of apparent gas wipe-out zones and the shallowing and possible emergence of the BSR on the seafloor (Figure 3). Geochemical analysis of piston cores and heatflow surveys were conducted to provide a complete set of parameters to confirm the presence of hydrates in this region. Specific piston core and heatflow locations are listed in Table 3.

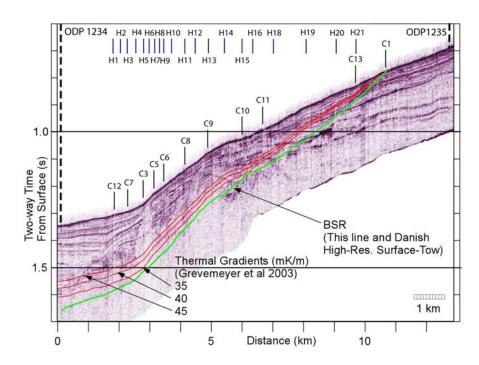


Figure 2: Piston core and heatflow site selection along the April 2003 DTAGS line.

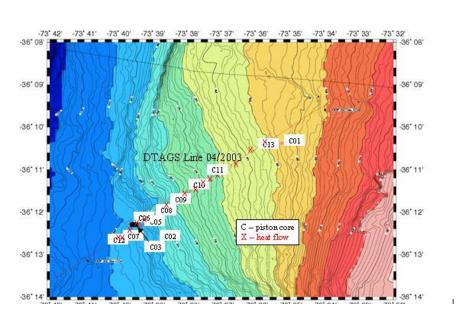


Figure 3: April 2003 DTAGS profile of mid Chilean coast used for selection of piston core and heatflow sample locations.

In the second region, points for piston coring and heatflow probing were based on Agassiz trawling during previous expeditions and results while trawling during this cruise (Table 4). The benthic sampling was around a mound that was due west of Concepción. Trawl samples yielded dense populations of a wide variety of benthic organisms, including chemosymbiotic fauna typically associated to gas seepage. Thorough navigation logging during this trawl assisted in the selection of piston core and heatflow stations (Figure 4).

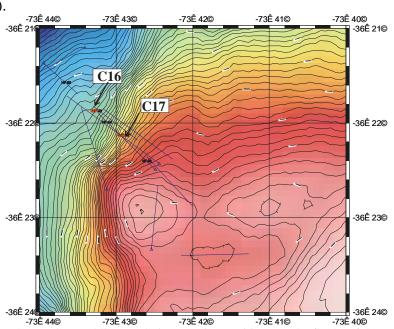


Figure 4: Hydrate mound Agassiz trawl lines and piston coring positions on the flanks of the mound.

Table 3: Piston core and heatflow locations and site water column depth.

Core #	Lat	Long	Depth	Comments
	(actual)	(actual)	(m)	
1	36 10.26	73 35.05	586	BSR at seafloor
2	36 12.53	73 38.57	883	center of wipeout
3	36 12.33	73 39.50	956	downslope edge of wipeout
4	36 12.31	73 39.28	926	center of wipeout/take 2
5	36 12.20	73 39.33	928	center of wipeout/take 3
6	36 12.13	73 39.15	922	upslope edge of wipeout
7	36 12.50	73 39.76	980	downslope of wipeout
8	36 11.90	73 38.80	854	upslope edge of wipeout
9	36 11.74	73 38.35	796	upslope from wipeout
10	36 11.41	73 37.75	758	2nd wipeout on slope
11	36 11.26	73 37.35	723	wipeout on slope
12	36 12.58	73 40.03	989	base of slope
13	36 10.38	73 35.72	597	BSR at seafloor
14	36 15.04	74 00.01	768	Tolten canyon
15	39 15.60	74 19.02	1935	Tolten canyon
16	36 22.00	73 43.00	780	flank of mound
17	36 21.87	73 43.25	848	base of mound

Table 3: continued

Heatflow#				
1	36 12.61	73 40.03	991	pc 12
2	36 12.53	73 39.92	985	between pc 12 and pc7
3	36 12.51	73 39.76	976	pc7
4	36 12.40	73 39.63	967	between pc7 and pc3
5	36 12.33	73 39.49	952	pc3
6	36 12.26	73 39.41	933	between pc3 andpc5
7	36 12.24	73 39.29	923	pc5
5_2	36 12.32	73 39.50	952	pc3
5_3	36 12.32	73 39.49	952	pc3
6_2	36 12.24	73 39.45	933	between pc3 and pc5
7_2	36 12.19	73 39.33	923	pc5
8	36 12.16	73 39.24	913	between pc5 and pc6
9	36 12.13	73 39.15	900	рсб
10	36 12.06	73 39.00	900	between pc6 and pc8
11	36 11.87	73 38.81	860	pc8
12	36 11.84	73 38.58	832	between pc8 and pc9
13	36 11.72	73 38.35	800	pc9
14	36 11.56	73 38.07	776	between pc9 and pc10
15	36 11.4	73 37.75	752	pc10
16	36 11.33	73 37.54	737	between pc10 and pc11
17	36 11.21	73 37.35	723	pc11
18	36 11.2	73 37.124	702	between pc11 and pc13
19	36 10.84	73 36.59	652	between pc11 and pc13
20	36 10.55	73 36.06	617	between pc11and pc13
21	36 10.34	73 35.73	597	pc13
22	36 21.40	73 43.65	900	Mound

Table 4: CTD and Agassiz trawl (AGT) positions.

CTD	Date	Lat	Long	Depth	GMT Time
#					
1	08.10.2004	36 12.09	73 39.06	900	8:54 PM
2	09.10.2004	36 10.36	73 35.63	586	4:18 PM
3	09.10.2004	36 10.39	73 35.67	593	5:00 PM
4	09.10.2004	36 10.38	73 35.16	563	6:30 PM
AGT#				(start-end)	
1	09.10.2004	36 11.90	73 39.80	990 - 989	1:35 AM
2	09.10.2004	36 12.16	73 39.15	906-1000	4:06 AM
3	10.10.2004	36 09.75	73 34.50	521-576	1:45 PM
4	10.10.2004	36 10.50	73 35.95	613-563	3:20 PM
5	10.10.2004	36 21.65	73 44.42	904-900	7:06 PM
6	11.10.2004	36 21.75	73 43.55	865-726	1:25 PM
7	11.10.2004	36 21.64	73 43.57	865-926	7:36 PM
8	11.10.2004	36 21.80	73 43.10	854-708	10:50 PM
9	13.10.2004	36 21.90	73 43.21	850-713	1:05 AM
10	14.10.2004	36 22.68	73 42.46	709-708	11:01 AM

11	14.10.2004	37 34.42	74 01.92	1445-1278	8:06 PM
12	16.10.2004	39 15.59	74 22.70	1939-1973	3:50 AM
13	20.10.2004	36 21.91	73 43.21	843-728	11:49 PM

V. PARAMETERS

Geochemical and heatflow data for this expedition was obtained with analysis of samples on board, as well as back at the laboratories. This cruise report focuses on data from the samples that were analyzed on board. Additional data will be combined with information in the cruise report for manuscript submissions to refereed journals. The selection of samples that were analyzed onboard depended on key data needed to assist in sample station selection and the ability to transport and operate instruments on the ship. The following list is of key parameters, scientist responsible for the sample analysis and analysis location.

- Dissolved methane concentration (J. Pohlman on board)
- Sediment microbial community diversity (L. Hamdan, NRL)
- Sediment organic carbon δ^{13} C and Δ^{14} C (J. Pohlman and R. Coffin, NRL)
- Sediment inorganic carbon δ^{13} C and Δ^{14} C (J. Pohlman and R. Coffin, NRL)
- Thermal gradient (J. Gardner on board)
- Thermal conductivity (J. Gardner on board)
- Heatflow (J. Gardner on board)
- Dissolved methane δ^{13} C (R. Coffin, NRL)
- DIC concentration (J. Pohlman on board)
- DIC δ^{13} C (R. Coffin, NRL)
- DIC Δ^{14} C (NRL, J. Pohlman)
- Sulfate concentration (J. Pohlman on board)
- Chloride concentration (J. Pohlman on board)
- Organic acids (L. Hamdan, NRL)
- Barium and Calcium concentration (I. Novosel, Rice University)
- Total sulfide concentration (I. Novosel, on board)
- Benthic fauna sorting and sampling (J. Sellanes and E. Quiroga, on board)
- Benthic fauna tissue δ^{13} C and δ^{15} N (J. Sellanes, UDEC)
- Faunal aerobic and anaerobic enzymatic activity (E. Quiroga, UDEC)

VI. EQUIPMENT AND INSTRUMENTS ON BOARD

This cruise incorporated a broad range of geophysical, geochemical and biological parameters. A large part of the chemical analysis was conducted on board providing data interpretation that assisted in the station selections. A list of specific on board instrumentation is followed with a series of photographs of the deck and laboratory activity. Specific methods are outlined in the following section.

A. On Board Equipment and Instruments

- Rosette/CTD/Niskin bottles
- Heatflow probe
- Ion Chromatograph Mass Spectrometer
- Piston Corer
- Coulometer
- Gas Chromatograph
- Spectrophotometer
- Two Agassiz trawls (AGT), 1.5 and 1 m mouth opening

B. Piston Coring









Figure 5: MILBAR Hydrotest, Inc. designed a new piston core that was tested for geochemical sampling during this cruise. The new design provided a more safe core delivery and retrieval protocol with changes in the messenger weight and triggering mechanism. Through the cruise there were 17 piston coring attempts resulting in 15 successful cores. Failures in the core barrels were suspected to result from the strength of the hydrate beds that resulted in broken and bent core pipes. The final piston core deployed over a hydrate bed required repair prior to deployment.

C. Core Processing





Figure 6: Cores sleeves were taken from the piston core system and prepared on the deck for the porewater press, onboard analysis and sample storage.

D. Onboard Geochemical Analysis

The onboard laboratory was equipped to press sediments for porewater samples with a 24 port pressure system. Instrumentation was used to measure methane, sulfate, dissolved inorganic carbon, sulfide and chloride concentrations.



Figure 7a: Ion chromatograph used to measure sulfate and chloride concentrations in porewater.



Figure 7b: Coulometer used to measure porewater DIC concentrations



Figure 7c: A gas chromatograph used to measure methane concentrations in porewater.



Figure 7d: A 24 port sediment press system to obtain porewater samples.

C. Heatflow





Figure 8: NRL's marine heat-flow probe system, designed and built by the Geological Survey of Canada, is designed to measure temperature gradients and in-situ thermal conductivity of sediments.

D. Sediment Agassiz Trawl









Figure 9: The Agassiz trawl was used to sample biological abundance and diversity in regions along the Chilean shelf that were thought to be rich in methane hydrates.

E. Water Column Sampling





Figure 10: A water sampling rosette equipped with a depth finder, CTD probes and 24 1-L Niskin bottles were used to sample the water column for methane transported from the sediments.

VII. METHODS

A. Piston Coring

Milbar Hydro-Test provided coring personnel, expertise and specialized coring equipment for the acquisition of fifteen (15) piston cores. Initially, the cruise plan was to collect twenty (20) cores however due to poor weather conditions only 17 deployments were made. Of the 17 deployments, two were lost due to broken core barrels. An aft deployable piston core developed with a hydraulically actuated cradle and sled system. The system included a cradle for deployment, tracks for movement on the deck, a hydraulic planetary chain drive that was operated with a hydraulic ram, planetary winch, and hydraulic pump, reservoir and power unit. The sled system was used to secure the piston core in a horizontal position while on deck and to lift the piston core into the vertical position once moved to the edge of the ship via a hydraulic ram. The sled system runs along two rails which secure the entire system to the deck. The sled was moved across the deck using a hydraulic planetary chain drive which doubled as a sled break in the stop position.

Piston cores built for this expedition included 3,000 lbs. lead piston core weights complete with trigger assemblies, trigger weights, wire terminations, piston immobilizers and high strength core barrels. The coring equipment has been designed for aft deployment such that the system may be used on multiple ships that may or may not be capable of side deployment.

B. Core Processing

Core liners were pulled out of the barrel, capped and placed in liner holders. They were measured and labeled on each section, on the end caps, with section number, top or bottom. Each section of the core liners was marked at 10cm intervals. Core cutting was started from the bottom of the core and section to minimize loss of CH₄ from the core. For each core the lead processing person decided the core sampling resolution as a function of the core size, sediment color and observed gas pockets.

The core was cut in 10cm sections with a pipe cutter. Before cutting the sections, a 3 ml syringe was used to remove 2 mls of sediment for porewater methane concentration from the top of the core section. The syringes were prepared by slicing the leur-lock fitting at the 0 ml mark to provide a small sub-core. The samples were extruded into 20ml vials, sealed with thick gauge septa. After the core was processed, 2 mls of water were added and the vials are inverted and frozen. Another set of sub-samples were collected, in a 5 ml syring at the top of each 10 cm section, for microbial community diversity analysis. In general, the sampling distance was not less than 10 cm or more than 30 cm. In total, approximately 400 samples were collected, placed in zip lock bags and stored in a freezer immediately.

C. Porewater

Press Loading and Squeezing - Whole round core sections, kept in the cut core liner were transported to the lab. Clean dry spatulas were used to scrape the surface sediment from the core and the surface material was discarded. Sediment from the interior of the core was scooped out and placed inside the body of the press. The press bodies were filled with sediment to maximum capacity in order to leave a minimum volume of air. A clean dental dam was place on the air inflow side of the press body to prevent free airflow through the core. The press bodies were capped and placed on the porewater press rack. Porewater was collected in a 60 ml syringe on the press outflow line. Pressure through the line was constant with nitrogen gas. Sediment from the press was placed on a sheet of ashed Al foil and frozen.

Porewater Processing - A minimum of 7 ml porewater per sample was required. Using the side port on a three-port stopcock, 1 ml was removed from the 60 ml syringe with a 10 ml syringe. The appropriate amount of Cline reagent was added to the 10 ml syringe. (See sulfide section for details). A 0.2 μ m syringe filter and a 21 gauge needle was placed on the 60 ml syringe. The contents of the syringe were placed into a scintillation vial. Using a 1 ml fixed volume pipetter, 2 ml (exactly) of the sample were transferred into the serum vial for DIC concentration. Vials were sealed with septa immediately. Then 2-3 ml was transferred into the serum vial for δ^{13} C-DIC. Next the rest of the vial was filled with N₂ sparged water. About 0.5 ml of headspace was left in the vial. Vials were sealed with Teflon septa immediately. Then 2 ml were transferred into the screw top vial for the ion analysis (SO⁻⁴ and Cl). The ion samples were refrigerated and DIC samples were frozen. If available, two 1.5 ml splits of each sample were taken for trace metal analysis. One split of each collected porewater sample was acidified with suprapure 65% HNO₃ in order to stabilize the chemical

speciation and prevent mineral precipitation. The loc-top micro-centrifuge vials were then sealed with parafilm tape and refrigerated.

D. Water Column Sampling

Water column samples were taken with a rosette platform carrying the CTD and 10 L Niskin bottles. Water for methane and DIC was poured into the bottles though a piece of bubble tubing placed over the end of the Niskin bottle faucet. This removes bubbles in the tubing and prevented oxidation of the methane in the water. Methane and DIC samples were filled into a dark 60 ml serum bottle, fixed with 2% mercuric chloride and placed in the refrigerator.

E. Laboratory Analysis

- 1. <u>Sulfate and Chloride</u> Sulfate and chloride were measured with a Dionex DX-120 ion chromatograph equipped with an AS-9HC column. Samples were diluted 1:50 (vol/vol) prior to analysis and measured against a 1:50 diluted IAPSO standard seawater (28.9 mM SO₄⁻², 559 mM Cl⁻). Chloride concentrations lower than values measured in seawater is used to interpret the present of melted hydrates in the core.
- 2. <u>Carbon Isotope Analysis</u> Stable carbon and radiocarbon isotope ratios are measure on methane from hydrates and in porewater, DIC in porewater and in organic and inorganic matter in the sediment. For stable carbon isotope (δ¹³C) analysis gas phase samples are run on a Finnigan Delta Plus Isotope Ratio Mass Spectrometer with a sample injection through a Varian GC. For DIC samples are prepared by placing the seawater in an argon gas evacuated serum bottle, sealing the water sample and adding HCl to transfer the DIC to carbon dioxide in the bottle head space. Methane samples are concentrated with a cryogenic trap prior to injection. Solid samples are analyzed using a CN combustion instrument with He carrier gas flowing into the isotope ratio mass spectrometer. The gases removed with a gas tight syringe and injected into the mass spectrometer. For radio carbon isotope analysis (Δ¹⁴C) samples in different carbon phases are combusted or acidified to CO₂ and concentrated in a cryogenic distillation line. The trapped CO₂ is converted to graphite for AMS analysis on the NRL system. δ¹³C and Δ¹⁴C analysis is applied to trace the variation in sources, where the values are calculated as:

$$D^n C = \left[\frac{R_s}{R_{std}} - 1\right] \times 1000$$
 (%)

where D^n is the carbon isotope ratio, R is the $^{13}C/^{12}C$ for stable carbon or $^{14}C/^{12}C$ for radiocarbon, s is the sample and std is the standard. For $\delta^{13}C$ analysis the standard is PeeDee Belmenite. For $\Delta^{14}C$ the standards are oxalic acid and ^{14}C dead coal.

3. <u>Porewater Methane Concentrations</u> - Concentrations of porewater methane were measured on board using a Shimadzu GC-14A gas chromatograph equipped with a Hayesep 0.80/100 column.

- 4. <u>Sediment Percent Organic Carbon</u> The sediment carbon content is measured by weighing dried sediments and sediments that have bicarbonates removed with a HCl bath. The sediment organic carbon content is measured with a Carlos-Erba 1100 CNS instrument.
- 5. <u>Porewater DIC Concentrations</u> DIC concentrations were measured on board through titration on a coulometer. All samples were measured in triplicate.
- 6. Barium and Calcium Analysis The analysis, planned to be conducted by I. Novosel at Rice University, Houston, Texas, is going to be used to determine the maximum and previous sulfate methane interface (SMI), as well as the correlation between the present day SMI and the elevated concentrations of Ba or the so called Ba fronts. It has been shown that in marine environments Ba will precipitate closely above the well established SO₄²⁻ depletion zone (Dickens, 2001). The barite will dissolve if SO₄²⁻ is completely removed within that zone, for example due to increased methane flux migrating from below. Thus, any precipitated Ba found above the present day SMI will indicate possible increased methane fluxes in the past that have pushed the SMI closer to the seafloor (Dickens, 2001). The sediment samples will be analyszed for the solid phase trace metal and other mineral content. The syringe samples were split, where the second half of the samples were archived for future analyses. Parameters on the digested samples will include Ba, Ca, K, Mg and Sr using a ICP-AES.
- 7. Organic Acids –To characterize metabolic transformation of methane in sediment collected along the Chilean Margin we will track the concentration of bulk dissolve organic carbon (DOC) in porewaters. To constrain important metabolites associated with bacteria transformation of methane we will measure short chain organic acids such as lactate and acetate so as to better understand the activity of sulfate reducing bacterial arrayed along the length of cores. DOC will be analyzed using a Q1000 Total Organic Carbon analyzer. Organic acids will be analyzed using a method developed by one of the study participants which utilizes liquid chromatography separation and mass spectrometry detection.
- 8. <u>Porewater Sulfide Concentrations</u> The Cline method was used for on board measurement of sulfide concentrations. Cline reagents were stored in dark bottles at 4°C. Samples were set for 20 minutes after addition of the Cline reagent. A spectrophotometer was set at 670 nm for sulfide concentrations. Triplicate samples were analyzed and tap water was used for blanks.
- 9. Sediment Microbial Community Diversity A study of microbial communities from sediments collected in hydrate-bearing regions was planned for onshore processing. This is designed to describe unique microbial communities found in methane hydrate containing sediments relative to neighboring locations depleted in hydrates. The study compares and contrast bacterial and archael groups arrayed along the depth of core samples which are positively identified to contain methane gas. This work is designed to compliment geo-chemical measurements made simultaneously using cultivation-independent 16s ribosomal DNA (rDNA) surveys which are not restricted by the need to

maintain *in situ* conditions. It is hypothesized that rapid shifts in community composition will occur on small spatial scales in and around the sulfate-methane interface of gas containing cores.

Retrieved core sediment are processed with sterile, DNA free methods in order to minimize exchange of foreign genetic material with core sub-samples. Approximately a 5ml sample of sediment is collected aseptically and frozen immediately after collection. Bacterial and archeal counts are performed using the acridine orange direct counting method on frozen samples. Genomic DNA is extracted from duplicate 0.5g samples of frozen core material using the Bio101® Systems FastDNA Spin Kit for soil. Small-subunit 16S rDNA are amplified by PCR, sequenced and submitted to GenBank for preliminary analysis using a ribosomal database in order to identify close phylogenetic relatives.

10. Water Column Methane Concentrations – Approximately 30 of water was taken from the field serum bottles with a 60 ml plastic syringes with a three way valve. Exact volumes were recorded. The remaining volume in the syringe was filled with nitrogen. The syringes were shaken two times for three minutes. The gases from the syringe were injected into a Shimadzu GC-14A gas chromatograph. Triplicates were measured on all samples. Water column methane concentrations were consistently low, ranging between 1 and 3 nm. These data are not presented in this report.

E. Heatflow

High resolution heatflow data profiles were collected, processed and interpreted. Using NRL's marine heat-flow probe system. The heatflow probe, data analysis package was designed and built by the Geological Survey of Canada to measure sediment temperature gradients and in-situ thermal conductivity. The length of probe was selected according to the "stiffness" of the sediments under investigation. NRL's probe is 3.5 meters long. Temperatures and temperature gradients within the sediment were measured by thermistors that are located at a known (30 cm) spacing within a small-diameter tube held in tension parallel to a solid steel strength member. Measurement of the thermal conductivity of the sediment was accomplished by allowing the probe to remain at rest in the sediment (typically for a period of 7 minutes) to allow dissipation of the frictional heating generated by the penetration of the probe, and then heating the probe and surrounding sediment by application of a known amount of energy (typically 600 joules/metre) to a heater wire paralleling the thermistors within the sensor tube. Analysis of the temperature decay following this period of energy input (or "heat pulse") yielded the conductivity of the sediment.

Other parameters, in addition to the temperatures in the probe were also logged. These include: pressure (water depth), water temperature, tilt, a stable reference resistance, and time. All parameters were logged in solid state memory. The probe was lowered at the beginning of a working day. After making a penetration into the sediments for thermal gradient measurements (and a conductivity measurement), the probe was raised clear of the bottom and moved to the next site for another penetration. The probe was returned to the

surface after five measurements were taken and data were downloaded and inspected for quality control purposes.

F. Sediment Agassiz Trawl

Benthic megafauna was sampled at 13 opportunities, using an Agassiz trawl (AGT) of 1.5 x 0.4 m mouth opening and 10 x 10 mm mesh size at the cod-end. Temperature, salinity and dissolved oxygen background information for the northernmost area was provided by a CTD (Seabird mod. 25). In addition, a Rosette was used to take water samples (Table 4).

A primary (onboard) processing of organisms consisted of general diversity, biomass and abundance estimations from each Agassiz trawl haul. Prior to sorting and preservation, images of fresh organisms were taken for later taxonomical purposes. Preservation for taxonomical analysis was done in a 4% solution of buffered formalin in filtered seawater. Samples for animal tissue stable isotope analysis were frozen (-20°C). Selected tissues for molecular and enzymatic activity analysis were preserved in absolute ethanol and liquid nitrogen, respectively.

Based on previous evidence we expect that the species assemblages associated with cold seeps off Chile are similar in structure to others reported elsewhere, but should bear an important number of endemic species, many of them still unknown to science. Stable carbon and nitrogen isotope signatures of the fauna will also be analyzed in order to determine the extent of the reliance of heterotrophic benthos in primary production derived from chemosynthesis. A long term goal of this first proposal is to start generating a database (based both on classical and molecular taxonomy) of the benthic fauna associated to methane seepage, in order to have a base line to assess possible impacts due to potential future methane resource exploitation. Megafaunal samples from samples were methane seepage could be occurring will be gathered using an Agassiz trawl. Geochemical and heatflow data are associated with the megafaunal samples.

VIII. PRELEMINARY RESULTS

A. Piston Coring

Station locations for the sediment cores are presented in Table 1. The piston core was deployed 13 times along the March-April 2003 DTAGS line and a total of 12 cores were retrieved (Figure 2). Two cores were retrieved at the base of a near by mound where bottom Agassiz trawls collected biological samples associated with methane seeps (Figure 3), and 1 core was collected in the canyon at a south-eastern location relative to the study site.

Piston core deployment was initiated with three 3 m core barrels. Due to problems maintaining stations, resulting from high seas and difficulty with ship positioning, considerable equipment loss was experienced in obtaining the fifteen piston cores. Core number 4 was lost when two of the three barrels were broken off at the sea floor after penetration. This resulted in the loss of a piston immobilizer, core catcher and cutter head. Because the initial cores were not over 6 meters in length and to prevent further loss of

coring equipment, the remainder of the piston cores were deployed with only two barrels. Coring operations continued without incident until core 15. Core 15 was retrieved with another broken barrel which was lost as the coring system was being brought back onto the deck. This barrel failure resulted in the loss of a core catcher, final piston immobilizer and cutter head. Using a damaged core barrel the crew of the Vidal Gormaz fabricated a new cutter head that was sufficient to continue coring operations. At this point the coring operations in the southern region were abandoned because of high wind and seas and the research was focused on coring on a mound discovered near the northern study site. The one remaining core pipe was installed and a non-break away piston was rigged for break-away using parts left over from the other piston immobilizers. One more core was collected and also resulted in a damaged core barrel. The barrels were then welded together by the crew of the Vidal Gormaz in order to continue coring operations. The last core collected penetrated approximately 1 meter of sediment that contained methane hydrates and required approximately 33,000 lbs. of pull-back tension to recover. The terminations used for these operations have a breaking strength of only 29,000 lbs. which resulted in considerable yielding of the steel and slippage of the bronze core attachment nut. In addition to yielding the termination, the trigger weight was also lost. Coring operations were then abandoned due to the risk of the entire system being lost during deployment and recovery.

B. Porewater Analysis

Core porewaters were measured for sulfate, sulfide, chloride, dissolved inorganic carbon (DIC) and methane concentrations in the analytical chemistry laboratory installed on the ship. Data from 3 to 5 meter piston cores is compared with the DTAGS data from April 2003 and heatflow data taken on the DTAGS line during this cruise. Comparison of these three data sets provided an evaluation of hydrate distribution through the study region.

For the following data review specific cores have been selected from the sampling regions to provide a comparison of variation in the porewater chemistry, within the slope transect, that will be compared to the DTAGS and heatflow data. Along the seismic line samples were taken above a gas wipeout zone, above regions with a strong BSR and where the BSR appears to shallow and outcrop toward the seafloor. Other piston core porewater data presented are from the region southeast of the DTAGS transect on a mound in a known biologically active region.

Porewater geochemical data are plotted for comparison of methane, sulfate, DIC and sulfide concentrations to assess the varying degrees of vertical methane fluxes and resulting anaerobic oxidation of methane (AOM) (Borowski et al., 1997). This methane cycle is microbiological,

$$CH_4 + SO_4^{2\text{-}} \longrightarrow HCO_{3\text{-}} + HS^{\text{-}} + H_20$$

where methane originating from deep vertical diffusion upward and shallow production is oxidized for biological energy and sulfate, available through downward diffusion from seawater, serves as the electron acceptor. This AOM results in reduction of sulfate to sulfide and oxidation of methane to carbonate in a region of the sediment referred to as the sulfate-

methane interface (SMI). Chloride data is included in the porewater analyses to trace segments of the piston cores that contained hydrates, with the assumption that chloride concentrations decrease in sections of the core that have dissociated hydrates through dilution by salt free water from melted hydrate. This regional data summary is followed with a comparison of each parameter from all 15 cores for an overview of the spatial variation in the parameters between the core locations.

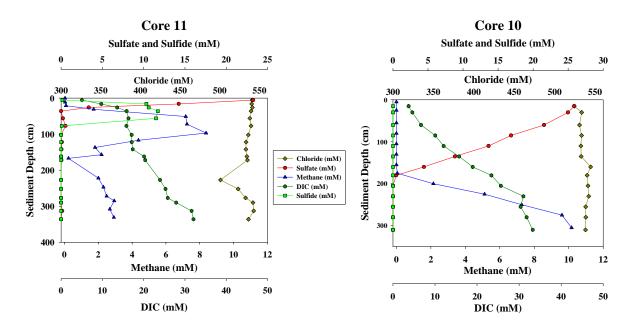


Figure 11: A comparison of core sulfate, methane, sulfide, dissolved inorganic carbon and chloride porewater samples taken along the previous DTAGS line. Core 11 was taken over a gas wipe out region and Core 10 was taken over the BSR. In both cases shallow sulfate and methane were observed. Profiles taken over the gas wipe out zone were substantially shallower.

The porewater methane, sulfate, DIC and sulfide profiles measured in the ship laboratory provide data to contribute to prediction of methane hydrates deep in the sediment. In regions where DTAGS data shows a strong BSR, there are shallow gradients for the sulfate and methane depletion that characterize the SMI range from 185 to 292 cm deep in the sediment. For an overview of the coring transect along the DTAGS line Core 10 was collected over the BSR (Figure 11). Porewater sulfate and methane profiles at this station were shallow with a SMI depth at 189 cm. A surprising result from this data was with the sulfate depletion, through the vertical profile, there was not an increase in the sulfide concentration. This observation on the vertical sulfide profile was consistent in many of the cores analyzed along this transect, with the exception of Core 11. Changes in the DIC concentration in the porewater were not large through the core (Figure 11). A more thorough summary of the DIC is presented in comparison between all cores taken during this cruise (presented below). Chloride concentrations in Core 10 did not vary through the vertical profile, indicating that hydrates were not in this core. This chloride profile was noted for all cores along the DTAGS line with the exception of Core 11.

Core 11 was taken in the center of one of the gas wipe out regions that was observed in the DTAGS seismic data. Here porewater parameters are dramatically different than observed for cores taken over the BSR (Figure 11). In this case the SMI was observed at 30 cm. In this shallow region an increase in the sulfide concentration was noted. Deeper in this core at 290 cm, a second methane peak is observed with a corresponding decrease in the chloride concentration. With no sulfate or sulfide present and the occurrence of decreased chloride and increased methane concentrations it is likely that a hydrate was present in this core and dissociated during transport back to the deck.

Core 14 was considered to be in a control region, south of the DTAGS profile, where the sediment was less shallow and a BSR was not measured in the seismic survey (Figure 12). For this region the sulfate minimum, predicted on a linear gradient to be 10.1 meters from data obtained with the core, was considerably deeper. The methane concentration through this core was measured to be between 0.0002 and 0.0032 mM and did not allow for the prediction of an SMI. A similar profile of porewater data was observed for Core 13 (Figure 12). In this region, the BSR appears to intersect and outcrop near the seafloor (Figure 2). Hydrates are not predicted in the deeper sediments by the geochemical data at this site, because the sulfate minimum is estimated to be at 7.3 meters and methane concentrations range from 0.0002 to 0.0006 mM. Core 13 was a repeat of Core 1 due to ship navigational inaccuracies. The porewater profiles for these cores were similar.

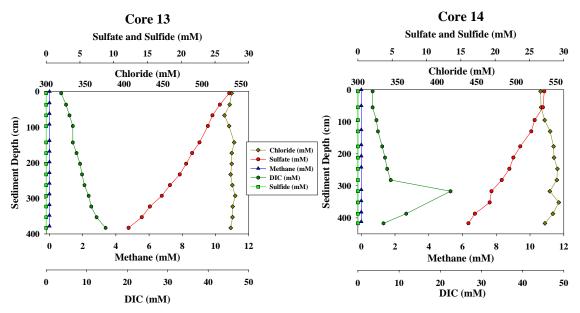


Figure 12: Porewater profiles for sulfate, methane, sulfide, dissolved inorganic carbon and chloride concentrations from 2 cores at less active regions. Core 14 was taken at a region south of the primary survey in a region with shallow sediments and no BSR. This serves as a control core. Core 13 was taken where the BSR appears to outcrop on the seafloor.

The other study region for piston coring was a 40 m subsea mound located to the south east of the primary field effort. This region was selected for coring because the biologists on board, from University of Concepión, observed a dense population of macro organisms on

the sediment surface during a series of Agassiz trawls. Core17 was taken at the base of the mound and Core 16 was taken on the flank of the mound. The porewater profiles of sulfate, methane and sulfide were substantially different than cores taken through the DTAGS line. Core 16 was observed to have the SMI at 219 cm (Figure 13) and the porewater sulfide concentrations were high and showed a large concentration associated with the disappearance of methane and sulfate. At the base of the mound, Core 17 had a very shallow SMI, estimated at 13.2 cm into the sediment (Figure 13). Also in this core was a strong relationship between the chloride and methane concentrations at 97 cm and 369 cm, respectively. Hydrate samples were obtained at these depths in this core.

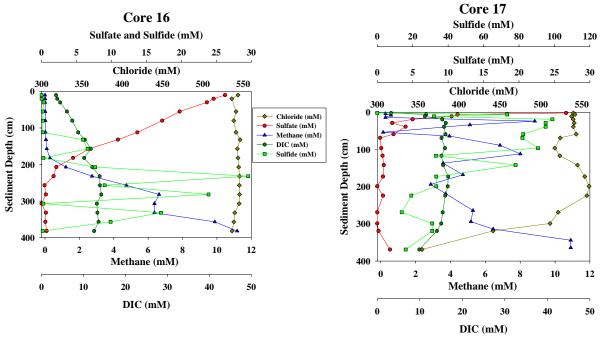


Figure 13: Porewater profiles for sulfate, methane, sulfide, dissolved inorganic carbon and chloride concentrations from sediment cores taken at the base of a mound located southeast of the DTAGS survey line. The location for these cores is presented in Figure 4

A comparison of the sulfate, methane, sulfide, chloride and DIC porewater data for all of the cores provides information on the variation between the coring sites. Sulfate profiles in the porewaters were observed to have three distinct regions (Figure 14). Cores 1, 13 and 14 showed the deepest sulfate gradients. The sulfate gradients in cores taken over the BSR identified on the DTAGS survey line and at the flank of the mound were intermediate with an SMI in the range of 185 cm to 292 cm. The shallowest SMI was observed in the center of the gas wipeout zone on the DTAGS survey line and at the base of the mound with values of 30 cm and 13.2 cm, respectively.

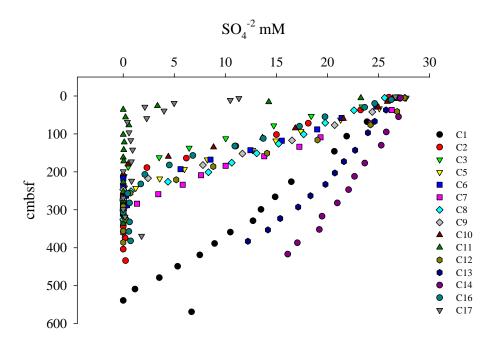


Figure 14: A comparison of porewater sulfate data for the 15 cores taken along the mid Chilean coast during October 2004.

Supporting data is observed with the other parameters. Porewater methane concentrations mirrored the sulfate profiles with the exception of Cores 1, 13, and 14 in which methane concentrations were low or at the limits of detection (Figure 15). Based on the chemical composition of porewater and hydrate gases the methane source is biogenic in origin (Appendix 1). Gas and hydrate samples had volume C1/C2 ratios ranging from 2376 to 5280. Dissolved gases in the porewaters ranged in the C1/C2 volume ratio from 18 to 93784 with a mean of 11683 for 61 of the 212 samples that contained measurable concentrations of C2 gas. Higher molecular weight gases were not present.

Sulfide was not observed in cores with the exception of Cores 11, 16 and 17 (Figure 16). It is expected that iron in the sediments resulted in precipitation of the sulfide to form iron sulfide. In conditions where high sulfide concentrations resulted from methane oxidation, iron became limited and sulfide remained in the porewater solution. Fluctuations in the chloride concentration in porewaters, analyzed to predict the presence of shallow methane hydrates trapped in the piston cores, was observed in Cores 11 and 17, at 250 cm and 320 to 370 cm, respectively (Figure 17). Methane hydrate samples were retrieved from Core 17 before total dissociation occurred.

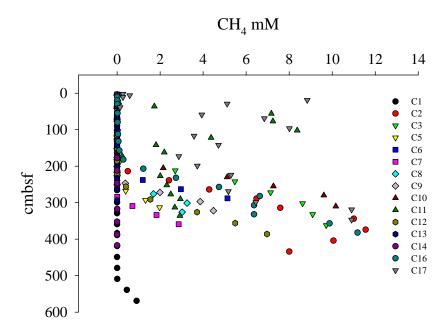


Figure 15: A comparison of porewater methane data for the 15 cores taken along the mid Chilean coast during October 2004.

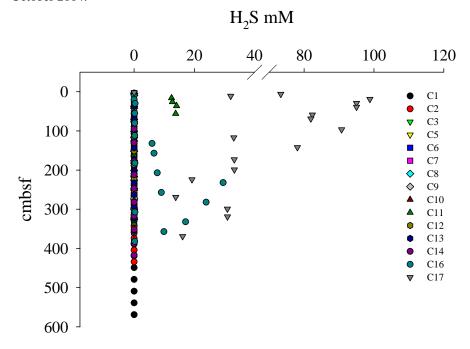


Figure 16: A comparison of porewater sulfide data for the 15 cores taken along the mid Chilean coast during October 2004.

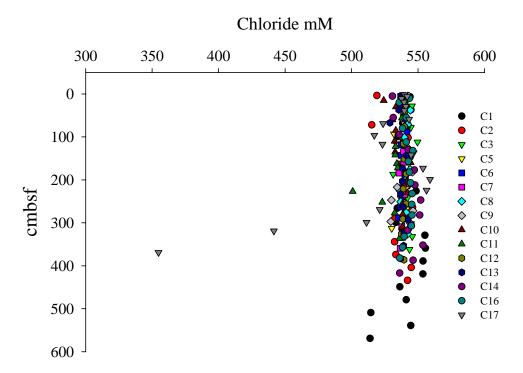


Figure 17: A comparison of porewater chloride data for the 15 cores taken along the mid Chilean coast during October 2004.

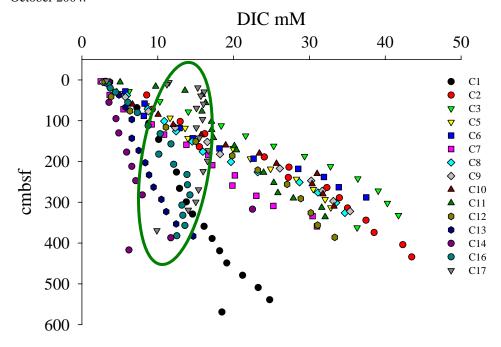


Figure 18: A comparison of porewater dissolved inorganic carbon data for the 15 cores taken along the mid Chilean coast during October 2004. Core 17 porewater DIC concentrations are circled to highlight the distinct difference in this profile.

Variation in DIC concentrations measured in the porewater corresponds to the methane oxidation observed in methane and sulfate profiles through the sediments. Control regions, Cores 1, 13 and 14 were observed to have the steepest slope with the lowest DIC concentrations (Figure 18). All other cores, with the exception of Core 17, had more DIC throughout the porewater profile. Core 17 was found to have a random distribution of DIC in the porewater that is likely the result of mixing of in the core caused by hydrate dissociation and porewater mixing.

B. Heatflow

Heatflow was conducted along the DTAGS and piston core transect. Selection included regions where the BSR was shallow and regions where apparent gas wipeout zones existed in the seismic data set. This heatflow data was collected at 21 sites along a NE-SW trending transect which ran between 36'10.38S, 73'35.72W and 36'12.50S, 73'3976W (Figure 2). An additional sample region was selected at the base of a 40 meter high sub-sea mound located at 36'22S, 73'43W where biologists from University of Concepción had located large concentrations of benthic organisms. Four of the five attempts at obtaining heatflow in this region were not successful due to probes being bent or shredded upon delivery into the sediment. The one successful heatflow site, that was intended as a control site, yielded a low heatflow value which is thought to result from shallow penetration into a hydrate bed.

There is a strong correlation between the heatflow values and the existence of gas wipe-out zones observed in the seismic data (Figure 19). Background heatflow values were measured to be in the range of 40 mW/m². Heatflow values more then three times the background level were observed over the apparent gas wipeout zone in the DTAGS line. Additionally, the BSR appears to be bowed upwards in this region. The piston cores in this same region, were found to have extremely shallow slopes for the methane and sulfate profiles with SMI depths measured between 25 and 250 cm. The combination of the heatflow and piston core data suggest a strong vertical migration of methane from deep sediments at this site where seismic data indicate a gas wipe out and possible perturbation of the BSR. This same phenomenon has been observed over seep sites in the Gulf of Mexico. Thermal modeling will be conducted, using the heatflow and thermal gradient information collected on this cruise, to try and simulate the apparent perturbation of the BSR.

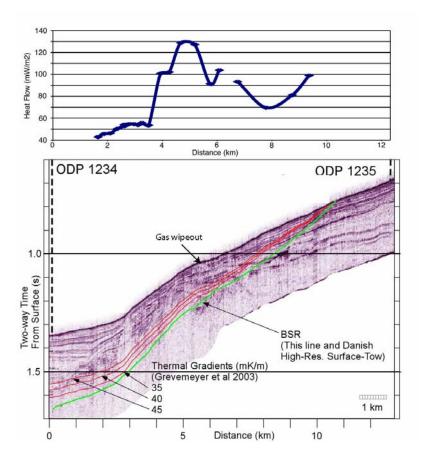


Figure 19. Heatflow value variations (top panel) along DTAGS high resolution seismic line. Note the apparent upward perturbation of the BSR where the arrow identifying the BSR is pointing.

C. Biological sampling

The total number of casts taken by the Agassiz trawl (AGT) was 13, with 12 containing abundant samples. Water depths (= mean depth between start and end of bottom transit) ranged from 521 to 1973 m (Table 4). The material collected in AGT's 5, 6, 7, 9, 10 and 13 indicated that at those sites or in the nearby areas methane should be escaping from the seafloor. While in most of these trawls carbonate breccia slabs were retrieved, indicating microbial processes associated to the anaerobic oxidation of methane in the sediments, AGT's 6, 7 and 9 were of particular interest because they contained live chemosymbiotic clams.

The biological composition and further details of each dredge are described in the Appendix 2, and a general outline of gross taxonomic composition and dominance is presented in Table 5. In summary, there is a remarkable increase in abundance, biomass and diversity of megafaunal communities in areas where methane is escaping from the seafloor. This is probably due to a trophic subsidy to the heterotrophic consumers by organic carbon derived from chemosynthesis. Carbon and nitrogen stable isotope analysis of selected tissue, sediment and suspended particulate material samples will be measured to verify this hypothesis. Another factor adding to enhanced biological activity could be related to the

formation of this carbonate reef, which create special and more complex habitats, resulting in increased biological diversity.

Regarding only chemosymbiotic species, at the moment it can be pointed out that at least six (probably seven) different species of bivalves were collected, most of them alive. Further studies are needed but with a high level of confidence it can be stated that all of them are new species to science. The diversity of the chemosymbiotic assemblage is also remarkable, the count so far is six different species, probably seven *Calyptogena* (probably 2 species), *Archivesica*, *Acharax*, *Thyasira*, *Conchocele* and *Lucinoma*. One of the *Calyptogena* species retrieved alive is actually being described based in shell fragments collected in a previous cruise in the area (Sellanes and Krylova, submitted). A very large and thick, unoccupied, tube (approx. 1 m long by 2 cm in diameter), with evidence of having been buried in the sulphidic sediment, resembling the tube of a vestimentiferan or siboglinid polychaete, was also found.

Table 5: Relative composition of the mega- and macrofauna off central Chile collected with Agassiz trawl (AGT) during the cruise

Taxa / Nro. of AGT	1	2	3	4	5	6	7	8	9	10	11	12	13
Foraminifera						1			1		++		1
Porifera		-				-			-	-			-
Cnidaria													
Hydroidea		-			-	-	-	-	-	-			-
Actinaria	++	-			+	+	+	+	-	-	-		-
Gorgonaria		_			_	+	_	+	+	++			+
Scleractinia		-			-	-	-	-	-	-			-
Nemertinea						_	_						
Mollusca													
Bivalvia	+	-	+	-	-	++	+	-	+	-	+		-
Aplacophora						· · ·	·		<u> </u>				
Gastropoda	+	+	+	-	+	+	+	+	-	-			++
Scaphopoda	<u> </u>	+	-	+	-	<u> </u>	<u> </u>	<u> </u>	-	-			
Polychaeta	1			- -									
Sedentaria	-	_	_	+	-	_	_		-	-	_		<u> </u>
Errantia	1	-	-	-	++	++	++	++	++	+	-		+
Pogonophora		-		_						-	_	Net did not touch the bottom	
Priapulida												otto	
Sipunculida			-	_		-	_	_		-		q	-
Echiurida		_	-	-		-	-	<u> </u>		-		₽	
		-										된	
Crustacea												ton	
Amphipoda												ot	
Isopoda							-	-	-			<u>ب</u>	-
Mysidacea												ë	
Stomatopoda												et	
Decapoda												_	
Natantia		-	+	+	-	+	+	+	+	-	-		+
Reptantia			-			-	-	-	-	-			-
Pantopoda									-				
Bryozoa		-			-	-	-	-	-	-			-
Brachiopoda		++				+	+	-	-	-			-
Echindermata													
Ophiuroidea		+		-	-	+	+	++	+	++	-		+
Asteroidea	+	+	+	+	-	-	-	+	+	+	+		-
Echinoidea													
Regularia						-	-	-	-	-	++		-
Irregularia		-											
Crinoidea								++					
Holothuroidea				-		-	-	-	-	-			-
Ascidacea		-				-	-		-	-			-
Pisces	-	-	+	+	+	-	-	-	-	-	+		-
Living chemsynthetic fauna							-						
Calyptogena gallardoi						5	2		5				2
Calyptogena (Ectenogena) sp.									1				
Acharax sp.							1						
Thyasira sp.							1		1				1

⁼ absent, - = scarce, + = common, ++ = dominant

IX. PRELIMINARY CONCLUSIONS

Final conclusions of this methane hydrate exploration will be based on data that will be completed in the thorough sample analysis. The preliminary data set presented in this report provides strong support for methane hydrate exploration in Chilean coastal waters. A previous seismic survey provides a profile with a high seismic resolution. Heatflow data taken through this region is used to confirm active vertical flow of methane from the BSR to the surface sediments where piston cores were taken. The geochemical data is used to confirm an active methane flux from the deep sediments. Based on the chemical composition of porewater and hydrate gases the methane source is biogenic in origin (Appendix 1).

The SMI has been used in surface sediment cores to predict the presence gas hydrates in the deep sediment (Borowski et al., 1999). In a thorough review of other sites, shallow SMIs were observed in nearshore regions off Cape Lookout Bight, NC and the Amazon shelf; between 3m and 20m water depths the SMI was measured to be in the range of 10 cm to 400 cm. In their study, coastal ocean sites with depths of 455 m to 1122 m found SMI to be approximately 10 m to 200 m deep in the sediment. The SMI along the mid Chilean coast was in a shallow range of 13 cm to 292 cm at water column depths between 723 m and 980 m. There is a correlation between the heatflow values and the existence of gas wipe-out zones observed in the seismic data (Figure 19). Heatflow values, observed over the apparent gas wipeout zone in the DTAGS line, are more then three times the background level. This observation was not consistent because the SMI and heatflow data did not always match high methane and heat gradients with the seismic data interpretation. Over the "wipeout' seismic line at the core 3 location the combination of porewater geochemical and heatflow data suggest that the core location is no longer an active site. Instead the seismic profiles at this location may result from deep carbonate deposits. Coupling of geophysical and geochemical data in this study indicate large methane hydrate deposits through the study regions.

The deep-sea fauna along the Chilean coast is scarcely known. Except for the general results of the *R/V Anton Bruun* cruise in the Southern Pacific (Menzies et al., 1973) and the studies of archibenthal fauna published by Andrade (1986), there are no detailed ecological studies on bathyal benthic communities. In this way, it is not surprising that the existence of methane seepage and associated chemosynthetic communities in the bathyal zone off central Chile has been realized only recently (Sellanes et al. 2004), based mainly in shell fragments of chemosymbiotic clams. The results obtained in the present cruise confirm the presence of living chemosynthetic communities associated to methane seepage in the area. Therefore, we expect that this data will open a new chapter in the understanding of composition and function of bathyal benthic communities off central Chile.

X. FUTURE GOALS

Subsequent efforts for investigation of the hydrate distribution along the mid Chilean coast will encompass completion of laboratory analysis of samples taken from the October 2004 cruise and integration with existing data from the March 2003 cruise. This data set will

assist in planning future methane hydrate exploration off the coast of Chile and at other coastal locations. Specific goals are listed in the following text.

- Analyze cores for porosity to assist in quantification of the vertical methane transport.
- Complete stable carbon isotope analysis on the porewater and hydrate methane.
- Complete stable carbon isotope analysis on the organic and inorganic carbon in the sediments of piston cores.
- Examine sediments from cores for variation in the microbial community diversity in regions with active and non active sulfate and sulfide profiles and regions with and without hydrates.
- Measure calcium and barium profiles in sediment core porewaters.
- Select and analysis sediment core carbon pools for radio carbon isotope analysis.
- Integrate DTAGS, core geochemistry data and heatflow profiles for a thorough evaluation of hydrate distribution in the primary study site.
- Develop and test thermal modeling of the BSR.
- Determine an approach for future sampling on mound where sampling was initiated.
- Evaluate other regions for future exploration.

XI. REFERENCES

Andrade, H. 1986. Observaciones biológicas sobre invertebrados demersales de la zona central de Chile. In: P. Arana (ed.). La pesca en Chile: 51-56.

Borowski, W. S., T. M Hoehler, M. J. Alperin, N. M Rodriguez and C. K. Paul. 1997. Significance of anaerobic methane oxidation in methane-rich sediments overlying the Blake Ridge gas hydrates. Proc. Ocean Drilling Prog. Scientific Results Vol. 164:87-99.

Borowski, W. S., C. K. Paull and W. Ussler III. 1999. Global and local variation of interstitial sulfate gradients in the deep-water, continental margin sediments: Sensitivity to underlying methane and gas hydrates. Mar. Geol. 159:131-154.

Dickens, G.R., 2001, Sulfate profiles and barium fronts in sediment on the Blake Ridge: Present and past methane fluxes through a large gas hydrate reservoir, Geochimica et Cosmochimica Acta, Vol. 65, No. 4, pp. 529-543.

Menzies, R., George, R., Rowe., G. 1973. Abyssal environment and ecology of the world ocean. Wiley-Interscience, New York, 467 pp.

Sellanes, J., Krylova, E. (2004) A new species of *Calyptogena* (BIVALVIA, Vesycomyidae) from a recently discovered methane seepage area off Concepción Bay, Chile (~36°S). Submitted to Journal of the Marine Biological. Association, United Kingdom.

Sellanes, J., Quiroga, E., Gallardo, V.A. 2004. First direct evidence of methane seepage and associated chemosynthetic communities in the bathyal zone off Chile. Journal of the Marine Biological. Association, United Kingdom. 84, 1065-1066

XII. DAILY ACTIVITY

10/04/04

 Departed for Valpariaso. US participants came from NRL, Washington DC, VIMS Glouscester Point Virginia, Rice University Houston Texas, and Milbar Hydrotest Inc. Shreveport Louisiana. Chilean scientists represented Catholic University of Valpariaso and University of Concepción.

10/05/04

• The US and Chilean scientists arrived in Valpariaso.

10/06/04

- Laboratories were washed to insure previous C¹⁴ labeled compound experiments did not contaminate the C¹⁴ natural abundance analysis.
- Chemistry lab equipment and heatflow monitoring equipment on was installed on board the *CNV Vidal Gomez* at the Navy Base in Valpariaso, Chile.
- Benthic sampling sleds were boarded and secured by scientists from University of Conception.
- Piston core equipment constructed and shipped by Milbar Hydrotest, Inc. was received and place on board.

10/07/04

- The piston core/heatflow deck sled was installed and weld to the ship fan tail.
- The piston core was setup in the deck sled cradle.
- Chemical needed for the analysis of porewaters were mixed at the Catholic University of Valpariaso.
- Departure from Valpariaso for piston coring at Region 1, furthest North in Figure 1.

10/08/04

• Two piston cores aimed at the center and down slope of the mound were taken and processed on the DTAGS line taken during March - April 2003. The first core, intended for the mound center was 1.5 km off the line. The second core was 0.5 m off the mound center. These are noted as cores 1 and 2, respectively.

10/09/04

- One piston core, Core 3, was taken at a site past center of the mound on the DTAGS line. This core was, on the selected site, was on the wipe out zone.
- Piston core 4 was taken at the center of the seismic wipe out zone. During this coring effort the ship vertical motion was about 15 ft. This resulted in breaking off and losing two of the three barrels on the piston core.
- Due to the high seas coring was cancelled for the remainder of the day.
- Surface sediment Agassiz trawls run through the late in the evening along the DTAGS seismic line.

10/10/04

- Seas were still too rough to accomplish the piston coring.
- 4 Agassiz trawls were run at locations along the mound to the southeast of the DTAGS line. From the trawls a large number of sea bottom shrimp, bivalves, fish, etc. Trawl sites included regions around a mound that had been previously surveyed by University of Concepción.

10/11/04

- Core down at 10:00 up at 11:00. This core was 49 m off the site chosen for core 2. Core 5. This is one core on the wipe out zone.
- Next core down at 13:00. This site was 910 m on the DTAGS line north of the wipe out zone. Core 6
- Next core down at 15:25 at a 1002 m down the line. Core 7
- Next core down at 17:30 at 870 m up the line. Core 8
- Agassiz trawling started after the coring around the mound region. High biologic abundance was observed at this site and living chemosymbiotic clams were retrieved

alive for the first time in a research cruise off the coast of Chile. The high biologic activity initiated conversation on coring in this region. The porewater chemistry data could show methane seepage supporting the surface benthic food chain.

10/12/04

- Core 9 down at site north of 8 at 08:30, near 800 m line. This core had a high gas concentration in the deeper segments.
- Core 10 set down at 10:30 near 750 m depth line. This core was placed on top of a DTAGS wipeout zone. It is important to talk to Warren Wood about the DTAGS interpretation. Through the following decisions for the core site selection there was not agreement between Joan Gardner and Juan Diaz about the BSR. Further conversation with Warren Wood would assist in understanding the heatflow and geochemistry data. heatflow from Joan Gardner will assist in determining the vertical methane flow and the wipe out zone. This was stated to be the region with the highest methane.
- Core 11 down at 14:15 this region is another potential wipe out zone. This core was the first with strong gas pockets in the core liner. Core liners were drilled at the gas pocket sites and sampled with a 60 ml syringe.
- Core 12 was deployed at 16:45 this is the furthest south control core. This was a control core taken at 1900 m.
- Core 13 furthest north at 600 m. This core is location where BSR meets the sediment surface. This is a repeat of core 1. Crew missed the site on the first attempt by 0.5 km. This core was thought to be an important site for vertical methane flux. Preliminary data from the GC during the evening found that the methane concentrations were remarkably low.
- Core 14 taken on the Agassiz trawl site. Three trawls were taken on an intersect point. This region had high number of animals and it is suggested that there is vertical methane flow. 3.5 kHz surface profile was taken through the region to predict carbonates to make certain that there was no carbonate damage to the piston core. After the piston core at 23:30 there was a 6 hr 3.5 kHz surface profile of the nearby mound. This data will be applied to future research. This core was originally cancelled because the sediment content could not be predicted and there was concern about losing the final piston core set up.

10/13/04

• Agassiz trawls taken near the mound along three intersecting line on the southern eastern region of the mound.

- Seismics of the mound and around the mound were taken at 3.5 kHz. Refined data showed two mounds. The larger mound had a 40 m slope on one side and a 10 m slope off the opposite side. Originally it was thought that the top of the mound was a large flat plateau. Finer resolution conducted during this survey found that the mound had two peaks.
- Decision not to core on the seismic lines around Mocha Island. Instead move further south to Canyon and previous seismic line from Diaz. The group rationale for this decision was that this region had not had a strong seismic survey, gas vents were east off the island in an unstable hydrate region, and the work on this site would not meet the NRL goal to integrate geophysics and geochemistry to survey coastal hydrate distribution.

10//14/04

- The ship traveled to the southern most site where a set of deep canyon seismic data had been surveyed for Juan Diaz's dissertation. The region studied with seismic data ranged from 780-3000 m deep.
- Core 14 was obtained at the shallow region of the seismic profile at 780 m. This core was on the deck at 09:30. This core is low on methane because of crust structure and shallow (100 m) sediments. Sulfate, sulfide and methane profiles provide a good control site to differentiate vertical flow and autochthonous methane production.
- For core 15 high seas resulted in a delay of coring. Cross seas were a problem to predict the waves. Core finally over at 17:00, depth of station 1900, This region was picked because of a wipe out zone in the middle of a BSR. The core was retrieved with a broken pipe. The rest of the coring day was cancelled. Dredge net was run through the night.

10/15/04

• With high seas and running short of time dedicated to coring plans were changed to return to the mound.

10/16/04

- Core 16 was taken at 2:00 below the mound in a region where dredging was occurring.. This coring site is at the cross section of two sled runs at the steep side of the mound. A core was obtained but the pipe was bent. The pipes were welded together for subsequent coring. The goal is a line of three cores with the third on the mound top.
- Core 17 was placed more toward the mound. The core dropped at 06:30. Pictures of the welding were taken. This core pulled 33,000 lbs on the pull out. The trigger weight was lost. The core was rich in methane hydrates, providing the first methane

hydrate samples retrieved off the coast of Chile. Further study of the cable swivel found that it had been pulled and that it was possible to lose the piston with a subsequent core.

• Core equipment was stored and the heatflow was set up on the coring winch track. Heatflow was conducted at the southern, deep end of the DTAGS and coring line.

10/17/04

- Nine heatflow stations were measured. A couple of stations were repeated several times.
- Heatflow penetration was only a meter because the winch would not free fall. The winch was run at 60 m min⁻¹.
- Seas picked up through the day. It was difficult to retrieve the heatflow probe.

10/18/04

- Heatflow was launched in high seas at 07:30. Sled delivery chain was broken because the cradle was moved in the up position. After release of the heatflow the chain link was replaced.
- Heatflow up at 2000 local. 9 stations completed

10/19/04

• Heatflow launched in high seas at 0830 local. Heatflow on deck at 1245 to to download data. Redeployed at 1345. Recovered at 2000 local. 8 stations completed.

10/20/04

- Heatflow deployed at 0830 local in high seas. Recovered at 1300 to download data.
 Thermistor string damaged and required replacement. Redeployed at 1430.
 Recovered at 1800 and discovered that the thermistor string was damaged again. End of heatflow operations. 8 stations completed
- Depart for mound to commence trawling at 2000 local. Arrive at mound site at 2100 local. Trawl deployed at 2130 local.

10/21/04

- Trawl recovered at 0230 local.
- Transit to port
- Arrive in Concepcion at 0800 local12:45.

Appendix 1: Piston core water data

				ı	l	1	l		ı	ı	1		1		1
Core	Porewater Sed Depth (cm)	Chloride (mM)	Chloride (mg/L)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	δ ¹³ C DIC	Gas Sample Depth Below Surface (cm)	CH ₄ (mM)	ng CH ₄ /g wet sed (ppbw)	C ₂ H ₆ (nM)	ng C ₂ H ₆ /g wet sed (ppbw)	C1/C2 (vol)	C1/C2 (mass)	SMI (cm)
1	7	544.0	19284	27.1	0.00	3.5	-9.70	0	0.0004	1.8	Bd	bd			555
1	68	538.4	19086	23.9	0.00	7.3	-14.37	63	0.0004	3.3	Bd	bd			
1	106	539.0	19108	21.9	0.00	8.8	-16.45	101	0.0007	4.3	Bd	bd			
1	146	544.1	19289	20.7	0.00	10.1	-18.10	141	0.0011	4.9	Bd	bd			
1	186	nd	nd	Nd	nd	nd	nd	181	0.0008	3.5	Bd	bd			
1	226	548.5	19444	16.5	0.00	12.5	-21.91	221	0.0007	3.1	Bd	bd			
1	266	534.3	18942	14.9	0.00	12.9	-23.54	261	0.0006	2.9	Bd	bd			
1	299	533.3	18906	13.5	0.00	13.8	nd	294	0.0006	2.8	Bd	bd			
1	329	555.1	19679	12.7	0.00	14.6	-25.65	324	0.0006	2.6	Bd	bd			
1	359	555.5	19693	10.5	0.00	16.1	-26.41	354	0.0005	2.5	Bd	bd			
1	389	553.7	19628	8.9	0.00	17.2	-27.94	384	0.0007	3.2	Bd	bd			
1	419	553.7	19627	7.5	0.00	18.2	-27.87	414	0.0008	3.6	Bd	bd			
1	449	536.3	19013	5.3	0.00	19.1	-28.68	444	0.0009	4.1	Bd	bd			
1	479	541.1	19182	3.5	0.00	21.2	-29.76	474	0.0032	14.6	Bd	bd		1	
1	509	514.5	18238	1.2	0.00	23.2	-30.33	504	0.0069	31.0	Bd	bd			
1	539	544.5	19303	0.0	0.00	24.8	-30.07	534	0.4514	2043.5	Bd	bd			
1	569	513.9	18217	6.7	0.00	18.5	-29.56	564	0.9072	4107.1	Bd	bd			
2	4	519.0	18400	26.0	0.00	3.2	-8.07	0	0.0003	1.3	Bd	bd			202
2	37	544.6	19308	23.2	0.00	8.5	-16.49	32	0.0022	9.8	Bd	bd			
2	72	515.2	18264	18.1	0.00	9.3	-19.26	67	0.0022	3.1	Bd	bd			
2	102	542.5	19231	15.0	0.00	13.0	-21.30	97	0.0090	40.8	Bd	bd			
2	132	540.3	19154	11.0	0.00	16.2	-21.14	127	0.0013	6.0	Bd	bd			
2	164	535.3	18978	6.2	0.00	15.5	-22.17	159	0.0084	37.9	Bd	bd			
2	189	540.1	19146	2.3	0.00	24.1	-22.84	184	0.0034	15.5	Bd	bd			
2	214	539.5	19126	0.0	0.00	27.3	-21.31	209	0.4954	2242.9	0.3	0.3	13061	6966	
2	239	540.3	19153	0.0	0.00	27.2	-16.40	234	2.4095	10908.8	Bd	bd	15001	0,00	
2	264	545.9	19351	0.0	0.00	32.3	-12.41	259	4.2813	19383.2	Bd	bd			
2	289	532.6	18882	0.0	0.00	34.0	-8.57	284	6.4794	29335.1	0.6	0.6	93784	50018	
2	314	537.9	19067	0.0	0.00	35.0	-7.56	309	7.5861	34345.5	0.9	0.9	72726	38787	
2	344	532.3	18871	0.0	0.00	37.5	-5.09	339	11.0017	49809.5	1.4	1.4	65760	35072	
2	374	533.3	18905	0.2	0.00	38.5	-2.71	369	11.5545	52312.6	1.5	1.5	63652	33948	
2	404	544.9	19317	0.0	0.00	42.3	-1.31	399	10.0587	45540.3	1.5	1.5	58697	31305	
2	434	542.1	19219	0.2	0.00	43.5	0.41	429	8.0031	36233.6	Bd	bd			
3	5	nd	nd	Nd	nd	nd	nd	0	0.0002	0.8	Bd	bd			257
3	28	545.4	19335	23.4	0.00	6.2	-16.15	23	0.0003	1.1	Bd	bd			
3	53	539.0	19109	18.4	0.00	10.3	-17.92	48	0.0003	1.6	Bd	bd			
3	78	544.6	19305	14.7	0.00	14.0	-19.69	73	0.0004	1.8	Bd	bd			
3	112	549.6	19482	10.0	0.00	18.4	-20.83	107	0.0005	2.4	Bd	bd			
3	137	546.7	19380	6.5	0.00	21.6	-20.91	132	0.0006	2.7	Bd	bd			
3	162	543.3	19259	3.5	0.00	25.3	-20.93	157	0.0011	4.8	Bd	bd			
3	187	531.3	18834	0.5	0.00	29.4	-20.74	182	0.1279	578.9	Bd	bd			
3	212	543.5	19268	0.1	0.00	32.8	-14.26	207	2.7016	12231.2	Bd	bd			
3	242	542.1	19218	0.1	0.00	36.4	-8.34	237	5.4714	24771.3	Bd	bd			
3	272	540.7	19167	0.0	0.00	39.1	-6.21	267	7.1355	32305.6	1.0	1.0	60198	32106	
3	302	544.6	19307	0.0	0.00	40.3	-6.74	297	8.6238	39044.0	1.2	1.2	58673	31292	
3	332	545.6	19342	0.0	0.00	41.7	-1.50	327	9.0922	41164.7	1.4	1.4	56640	30208	
3	362	543.5	19269	0.0	0.00	36.3	0.33	357	9.7220	44015.8	1.5	1.5	54994	29330	

			I	ĺ	l	l	l	Gas	l		I		Ī	1	
								Sample							
	Porewater							Depth		ng		ng			
	Sed						12	Below		CH ₄ /g		C_2H_6/g			
	Depth	Chloride	Chloride	Sulfate	Sulfide	DIC	δ ¹³ C	Surface	CH ₄	wet sed	C_2H_6	wet sed	C1/C2	C1/C2	SMI
Core	(cm)	(mM)	(mg/L)	(mM)	(mM)	(mM)	-7.08	(cm)	(mM)	(ppbw)	(nM)	(ppbw)	(vol)	(mass)	(cm) 256
5	5	540.2	19150	27.7	0.00	3.0	-13.48	0	0.0002	1.0	Bd	bd			230
5	33	541.2	19186	25.1	0.00	5.0		28	0.0002	0.9	Bd	bd			
5	63	538.5	19090	21.3	0.00	8.5	-17.08	58	0.0002	1.1	Bd	bd			
5	93	531.9	18855	17.4	0.00	11.6	-19.08	88	0.0003	1.4	Bd	bd			
5	118	534.0	18929	14.9	0.00	13.6	-19.29	113	0.0003	1.6	Bd	bd			
5	143	541.4	19192	12.7	0.00	14.0	-19.90	138	0.0004	1.8	Bd	bd			
5	168	534.9	18961	8.2	0.00	19.9	-20.45	163	0.0005	2.2	Bd	bd			
5	193	540.9	19174	6.0	0.00	22.2	-21.09	188	0.0005	2.4	Bd	bd			
5	218	541.5	19197	3.6	0.00	24.9	-20.91	213	0.0009	3.9	Bd	bd			
5	243	537.0	19036	1.2	0.00	28.3	-21.55	238	0.0023	10.6	Bd	bd			
5	268	541.4	19192	0.0	0.00	30.5	-19.86	263	0.3962	1793.8	Bd	bd		ļ	
5	293	539.5	19124	0.0	0.00	32.1	-16.61	288	1.3213	5982.2	Bd	bd			
5	313	530.2	18796	0.0	0.00	32.8	-14.51	308	1.9743	8938.5	Bd	bd			
6	6	536.9	19034	26.6	0.00	3.5	-10.05	0	0.0002	1.0	Bd	bd			206
6	28	538.6	19093	24.8	0.00	5.7	-14.50	23	0.0002	1.1	Bd	bd			
6	58	540.0	19143	21.4	0.00	8.3	-16.80	53	0.0003	1.2	Bd	bd			
6	88	541.6	19201	19.0	0.00	8.2	-18.26	83	0.0003	1.5	Bd	bd			
6	118	537.5	19053	15.5	0.00	12.9	-19.05	113	0.0023	10.5	Bd	bd			
6	143	537.4	19051	12.5	0.01	14.6	-21.06	138	0.0004	1.9	Bd	bd			
6	168	537.3	19046	8.5	0.00	18.1	-20.02	163	0.0004	1.8	Bd	bd			
6	193	540.5	19162	5.6	0.00	22.6	-20.93	188	0.0009	4.1	Bd	bd			
6	218	535.7	18989	0.0	0.00	28.5	-20.64	213	0.0166	75.3	Bd	bd			
6	238	537.9	19070	0.0	0.00	31.9	-16.94	233	1.1952	5411.3	Bd	bd			
6	263	536.7	19026	0.3	0.00	33.9	-12.02	258	2.9669	13432.3	Bd	bd			
6	288	535.2	18973	0.4	0.00	37.5	-7.89	283	5.1309	23230.1	Bd	bd			
7	4	538.3	19084	26.8	0.00	2.5	-4.55	0	0.0001	0.6	Bd	bd			297
7	37	539.8	19138	26.3	0.00	3.7	-8.65	32	0.0005	2.5	Bd	bd			
7	72	542.0	19215	24.2	0.00	5.5	-13.79	67	0.0003	1.3	Bd	bd			
7	109	540.4	19158	19.3	0.00	9.2	-17.86	104	0.0004	1.6	Bd	bd			
7	134	539.1	19110	17.2	0.00	10.8	-18.82	129	0.0005	2.1	Bd	bd			
7	159	539.3	19117	13.8	0.00	13.8	-20.47	154	0.0006	2.6	Bd	bd			
7	184	535.7	18989	10.0	0.00	16.7	-21.31	179	0.0007	3.0	Bd	bd			
7	209	543.4	19265	7.6	0.00	17.2	-21.93	204	0.0006	2.9	Bd	bd			
7	234	539.9	19139	5.8	0.00	20.2	-22.53	229	0.0009	4.3	Bd	bd			
7	259	538.4	19087	3.4	0.00	19.8	-23.07	254	0.0024	11.0	Bd	bd			
7	284	541.0	19179	1.3	0.01	23.0	-23.40	279	0.0064	28.8	Bd	bd			
7	309	537.8	19066	0.0	0.03	25.2	-20.81	304	0.7151	3237.7	Bd	bd			
7	334	538.3	19083	0.0	0.00	30.4	-15.40	329	1.8332	8299.8	Bd	bd			
7	359	536.6	19022	0.0	0.00	31.0	-13.80	354	2.8638	12965.8	Bd	bd			

						I		Gas	I	I	I	1	Ī	1	1
								Sample							
	Porewater							Depth		ng		ng			
	Sed	a		G 10	G 101	D.C.	213.0	Below	ar.	CH ₄ /g		C_2H_6/g	G1 (G2	G4 /G2	a
Core	Depth (cm)	Chloride (mM)	Chloride (mg/L)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	δ ¹³ C DIC	Surface (cm)	CH ₄ (mM)	wet sed (ppbw)	C ₂ H ₆ (nM)	wet sed (ppbw)	C1/C2 (vol)	C1/C2 (mass)	SMI (cm)
8	5	542.2	19220	25.6	0.00	3.0	-7.33	0	0.0002	1.0	Bd	bd			264
8	38	544.2	19292	22.6	0.00	5.9	-14.46	33	0.0008	3.7	Bd	bd			
8	71	542.4	19227	19.8	0.00	8.7	-21.50	66	0.0004	1.9	Bd	bd			
8	101	539.7	19134	17.7	0.00	10.9	-18.55	96	0.0115	52.3	Bd	bd			
8	126	542.4	19228	15.2	0.00	12.4	-20.34	121	0.0003	1.5	Bd	bd			
8	151	543.1	19254	13.1	0.00	14.6	-19.88	146	0.0007	3.2	Bd	bd			
8	176	544.0	19286	10.6	0.00	16.0	-20.05	171	0.0005	2.4	Bd	bd			
8	201	540.4	19156	8.3	0.00	19.7	-20.60	196	0.0005	2.2	Bd	bd			
8	226	536.6	19024	4.4	0.00	23.2	-21.54	221	0.0007	3.4	Bd	bd			
8	251	537.0	19036	0.8	0.00	28.7	-21.75	246	0.0031	14.2	Bd	bd			
8	276	541.1	19182	0.0	0.00	31.1	-17.68	271	1.6899	7651.1	Bd	bd			
8	301	544.2	19293	0.0	0.00	33.5	-13.46	296	3.2528	14726.8	2.1	2.1	13157	7017	
8	326	542.2	19220	0.0	0.00	34.7	-10.86	321	3.0244	13692.7	Bd	bd			
9	5	543.1	19252	27.6	0.00	2.8	-7.01	0	0.0002	1.0	Bd	bd			232
9	42	538.8	19101	24.4	0.00	5.7	-14.43	37	0.0002	1.0	Bd	bd			
9	77	540.1	19145	20.7	0.00	8.8	-18.09	72	0.0004	1.9	Bd	bd			
9	117	540.0	19144	16.5	0.00	12.3	-20.38	112	0.0004	1.7	Bd	bd			
9	152	541.6	19201	11.7	0.00	16.5	-20.07	147	0.0007	3.2	Bd	bd			
9	182	545.8	19349	7.8	0.00	18.2	-20.91	177	0.0004	1.9	Bd	bd			
9	217	534.3	18942	2.4	0.00	26.1	-21.46	212	0.0009	3.9	Bd	bd			
9	247	530.0	18787	0.0	0.00	30.2	-20.36	242	0.3804	1722.3	Bd	bd			
9	272	546.2	19362	0.0	0.00	31.7	-14.87	267	1.9903	9010.8	Bd	bd			
9	297	529.5	18772	0.0	0.00	33.2	-12.18	292	3.8649	17498.3	Bd	bd			
9	322	538.6	19092	0.2	0.00	35.4	-8.47	317	4.4760	20264.9	0.6	0.6	64787	34553	
10	15	524.2	18582	25.9	0.00	3.7	-11.78	5	0.0006	2.7	Bd	bd			193
10	30	533.3	18907	25.0	0.00	4.6	-16.06	25	0.0003	1.2	Bd	bd			
10	60	530.8	18815	21.6	0.00	6.7	nd	55	0.0003	1.5	Bd	bd			
10	85	533.3	18904	16.8	0.00	10.1	-23.67	80	0.0004	2.0	Bd	bd			
10	110	532.4	18875	13.6	0.00	12.0	-25.03	105	0.0007	3.3	Bd	bd			
10	135	532.8	18886	8.8	0.00	15.7	-26.54	130	0.0008	3.4	Bd	bd			
10	160	544.5	19301	4.4	0.00	19.0	-27.69	155	0.0013	5.8	0.6	0.6	18	9	
10	180	540.1	19147	0.5	0.00	23.4	-27.71	175	0.0498	225.3	1.1	1.1	401	214	
10	205	541.2	19186	0.0	0.00	25.7	-20.17	200	2.1455	9713.5	2.4	2.4	7471	3984	
10	230	542.1	19218	0.0	0.00	31.0	-14.57	225	5.1166	23165.0	4.4	4.4	9900	5280	
10	255	538.4	19086	0.0	0.00	30.4	-9.94	250	7.2668	32899.9	6.2	6.2	9980	5323	
10	280	538.5	19090	0.0	0.00	31.8	-7.56	275	9.6081	43500.2	8.061	8.06132	10118	5396	
10	310	538.1	19077	0.0	0.00	33.2	-3.84	305	10.1663	46027.3	8.521	8.521309	10128	5401	
10	210	220.1	27011	J.0	3.00	33.2	l	505	10.1003	10027.3	5.521	3.321307	10120	1 3 101	

								Gas							
	ъ.							Sample							
	Porewater Sed							Depth Below		ng CH ₄ /g		ng C ₂ H ₆ /g			
	Depth	Chloride	Chloride	Sulfate	Sulfide	DIC	$\delta^{13}C$	Surface	CH_4	wet sed	C_2H_6	wet sed	C1/C2	C1/C2	SMI
Core	(cm)	(mM)	(mg/L)	(mM)	(mM)	(mM)	DIC	(cm)	(mM)	(ppbw)	(nM)	(ppbw)	(vol)	(mass)	(cm)
11	6	540.5	19160	23.3	0.20	5.0	-29.95	0	0.0319	144.4	1.029	1.029227	263	140	31
11	16	540.1	19148	14.3	12.41	9.7	-44.32	11	0.0409	185.4	1.5	1.5	237	126	
11	26	541.1	19181	3.4	12.73	13.6	-49.45	21	0.0891	403.4	3.0	3.0	256	136	
11	36	539.3	19119	0.0	14.08	15.9	-45.09 -39.90	31	1.7297	7831.3	11.3	11.3	1305	696	
11	56	537.8	19067	0.2	13.79	16.3	-39.90	51	7.1714	32468.1	20.31	20.30855	2998	1599	
11	77	539.3	19117	0.5	0.09	15.8	-31.91	72	7.2437	32795.3	18.9	18.9	3261	1739	
11	102 122	535.9	18996 18899	0.0	0.01	17.1 17.1	-24.21	97	8.3738	37911.9 19788.3	21.3	21.3	3330 2924	1776	
11	142	533.1 532.9		0.1	0.01	17.4	-13.40	117 137	4.3707	8196.5	12.7	12.7	2322	1559	
11	162	534.1	18890 18934	0.1	0.00	20.1	-10.21	157	1.8104 2.1927	9927.3	6.6 7.4	6.6 7.4	2515	1238 1342	
11	172	534.1	18934	0.0	0.00	20.1	-9.21	167	0.2343	1061.0	6.9	6.9	286	1542	
11	227	500.9	17756	0.0	0.00	24.0	-5.07	222	2.0048	9076.7	5.894	5.893618	2888	1540	
11	252	523.1	18544	0.0	0.00	25.3	-3.31	247	2.3049	10435.1	6.917	6.917095	2829	1509	
11	277	532.5	18877	0.0	0.00	25.8	-3.50	272	2.4921	11282.9	6.066	6.066114	3487	1860	
11	290	541.8	19206	0.0	0.00	27.9	-1.68	285	2.9423	13321.1	6.3	6.3	3971	2118	
11	313	542.6	19236	0.1	0.00	31.6	-0.24	308	2.6818	12141.8	6.0	6.0	3814	2034	
11	336	536.1	19005	0.0	0.00	32.1	1.00	331	2.9191	13215.9	6.549	6.549104	3784	2018	
12	5	539.2	19115	27.5	0.00	3.0	-7.17	0	0.0003	1.4	Bd	bd			274
12	41	540.0	19143	26.8	0.00	3.9	-8.67	36	0.0010	4.3	Bd	bd			
12	76	539.8	19137	24.2	0.00	6.3	-14.46	71	0.0015	6.9	Bd	bd			
12	116	539.0	19109	19.0	0.00	11.1	-18.31	111	0.0009	3.9	Bd	bd			
12	151	539.6	19127	14.1	0.00	15.0	-20.52	146	0.0009	4.2	Bd	bd			
12	186	541.2	19185	8.8	0.00	19.8	-22.05	181	0.0012	5.3	Bd	bd			
12	221	538.8	19101	5.2	0.00	23.2	-22.71	216	0.0017	7.9	Bd	bd			
12	256	541.0	19180	0.7	0.00	27.1	-23.77	251	0.4106	1858.8	Bd	bd			
12	291	538.5	19091	0.0	0.00	28.9	-19.80	286	1.5480	7008.3	Bd	bd			
12	326	537.5	19055	0.2	0.00	30.2	-14.82	321	3.7143	16816.2	Bd	bd			
12	356	538.9	19103	0.0	0.00	31.1	-11.85	351	5.4904	24857.7	Bd	bd			
12	386	539.4	19123	0.0	0.00	33.3	-10.31	381	6.9667	31541.5	Bd	bd			
13	5	538.1	19075	27.1	0.00	3.7	-9.86	0	0.0004	1.7	Bd	bd			733
13	37	535.5	18983	25.7	0.00	4.9	-10.91	32	0.0005	2.0	Bd	bd			
13	67	528.9	18748	24.6	0.00	5.8	-12.44	62	0.0004	1.9	Bd	bd			
13	97	534.8	18959	24.0	0.00	6.6	-15.37	92	0.0006	2.7	Bd	bd			
13	143	541.4	19191	22.7	0.00	6.6	-15.97	138	0.0004	1.9	Bd	bd			
13	173	538.2	19080	21.6	0.00	7.5	-16.64	168	0.0004	1.8	Bd	bd			
13	203	538.2	19078	20.7	0.00	8.4	-18.08	198	0.0004	2.0	Bd	bd			
13	233	536.8	19028	19.8	0.00	8.9	-18.57	228	0.0002	1.0	Bd	bd			
13	263	538.9	19104	18.3	0.00	9.5	-19.62	258	0.0005	2.2	Bd	bd			
13	293	542.6	19235	17.1	0.00	10.5	-20.75	288	0.0002	1.1	Bd	bd			
13	323	539.4	19120	15.4	0.00	11.1	-21.61	318	0.0003	1.2	Bd	bd			
13	353	539.2	19114	14.2	0.00	12.4	-22.63	348	0.0003	1.5	Bd	bd			
13	383	537.0	19035	12.2	0.00	14.7	-23.63	378	0.0005	2.2	Bd	bd			

Core	Porewater Sed Depth (cm)	Chloride (mM)	Chloride (mg/L)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	δ ¹³ C DIC	Gas Sample Depth Below Surface (cm)	CH ₄ (mM)	ng CH₄/g wet sed (ppbw)	C ₂ H ₆ (nM)	ng C ₂ H ₆ /g wet sed (ppbw)	C1/C2 (vol)	C1/C2 (mass)	SMI (cm)
14	5	530.7	18813	27.2	0.00	3.6	-9.33	0	0.0002	0.9	Bd	bd			1011
14	55	531.3	18835	27.0	0.00	3.6	-8.03	50	0.0002	0.7	Bd	bd			
14	95	535.8	18995	25.8	0.00	4.5	-11.40	90	nd	nd	Nd	nd			
14	130	542.7	19240	25.3	0.00	4.9	-13.06	125	0.0002	1.1	Bd	bd			
14	177	547.2	19397	23.7	0.00	5.9	-14.95	172	0.0003	1.6	Bd	bd			
14	212	547.7	19415	22.7	0.00	6.6	-16.16	207	0.0004	1.7	Bd	bd			
14	247	552.0	19568	22.1	0.00	7.1	-18.54	242	0.0002	1.1	Bd	bd			
14	282	551.2	19542	21.0	0.00	8.0	-16.99	277	nd	nd	Nd	nd			
14	317	542.3	19224	19.5	0.00	22.5	-18.44	312	0.0015	6.7	Bd	bd			
14	352	553.7	19627	19.2	0.00	nd	-23.04	347	0.0003	1.2	Bd	bd			
14	387	546.3	19366	17.1	0.00	11.7	-19.30	382	0.0002	1.0	Bd	bd			
14	417	536.2	19009	16.1	0.00	6.2	-19.71	412	0.0032	14.5	Bd	bd			
16	10	543.6	19269	26.2	0.0	3.5	-18.83	10	0.005	20.7	53.5	0.5	86	46	295
16	20	535.9	18996	24.6	0.0	3.7	-27.94	20	0.006	28.7	30.5	0.3	208	111	
16	30	nd	nd	23.6	0.3	4.4	-29.91	30	0.009	38.9	61.0	0.5	141	75	
16	55	541.1	19182	19.8	0.2	6.1	-38.15	55	0.015	66.4	198.5	1.7	74	39	
16	80	538.3	19082	17.3	0.2	7.3	-41.63	80	0.021	95.6	330.5	2.8	64	34	
16	112	541.1	19182	13.7	0.2	8.7	-44.91	112	0.037	167.7	930.0	7.9	40	21	
16	132	546.0	19357	10.9	5.9	10.3	-47.57	132	0.058	264.3	1147.4	9.7	51	27	
16	157	542.7	19240	6.8	6.6	11.7	-49.97	157	0.104	471.4	1545.7	13.1	67	36	
16	182	543.5	19268	4.5	0.3	10.1	-50.08	182	0.286	1295.0	1832.9	15.6	156	83	
16	207	544.4	19297	2.1	7.7	12.1	-48.71	207	1.218	5512.6	2611.8	22.2	466	249	
16	232	545.5	19339	1.7	29.5	13.9	-45.19	232	2.737	12393.5	3070.4	26.1	892	475	
16	257	545.2	19328	0.4	9.0	13.9	-42.56	257	4.736	21439.9	4160.2	35.3	1138	607	
16	282	545.4	19336	0.6	23.9	14.2	-39.78	282	6.637	30046.8	4823.3	40.9	1376	734	
16	307	545.0	19320	0.0	0.3	13.2	-37.30	307	6.366	28823.3	4263.8	36.2	1493	796	
16	332	539.6	19127	0.6	17.1	13.3	-34.60	332	6.362	28805.6	4089.7	34.7	1556	830	
16	357	538.4	19085	0.5	9.9	13.6	-33.29	357	9.879	44727.7	5888.1	50.0	1678	895	
16	382	536.2	19008	0.7	0.2	12.5	-31.59	382	11.179	50612.3	6295.2	53.4	1776	947	

Core	Porewater Sed Depth (cm)	Chloride (mM)	Chloride (mg/L)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	δ ¹³ C DIC	Gas Sample Depth Below Surface (cm)	CH ₄ (mM)	ng CH ₄ /g wet sed (ppbw)	C ₂ H ₆ (nM)	ng C ₂ H ₆ /g wet sed (ppbw)	C1/C2 (vol)	C1/C2 (mass)	SMI (cm)
17	2	539.8	19137	26.6	0.0	3.3	-20.02	4	0.269	1218.7	1112.2	9.4	242	129	186
17	6	541.8	19208	11.3	73.3	11.5	-48.72	8	0.583	2640.8	2212.9	18.8	264	141	
17	11	537.6	19057	10.5	32.1	11.2	-49.84	14	0.271	1227.5	2898.3	24.6	94	50	
17	19	539.6	19128	5.0	98.9	15.3	-52.65	24	8.837	40008.0	5317.1	45.1	1662	886	
17	29	540.9	19174	2.1	95.0	16.1	-43.55	34	5.117	23165.4	5596.8	47.5	914	488	
17	39	539.7	19131	4.0	95.0	15.7	-44.08	54	0.137	621.8	951.0	8.1	144	77	
17	59	543.3	19260	2.3	82.4	16.0	-39.49	64	3.938	17829.3	1042.4	8.8	3778	2015	
17	69	523.7	18567	0.4	81.9	15.1	-32.25	89	6.844	30986.8	1666.9	14.2	4106	2190	
17	97	517.1	18333	0.6	90.7	15.9	-30.16	112	8.009	36260.4	1164.3	9.9	6879	3669	
17	117	523.2	18548	0.7	33.1	15.1	-27.58	137	3.576	16187.9	636.0	5.4	5622	2998	
17	142	544.8	19313	0.9	78.1	15.5	-25.56	168	4.714	21343.0	852.1	7.2	5532	2951	
17	173	553.7	19629	0.8	33.2	16.7	-22.14	194	2.870	12995.0	561.5	4.8	5112	2726	
17	199	559.0	19817	0.0	33.3	16.6	-19.97	219	3.728	16876.8	681.4	5.8	5471	2918	
17	224	556.4	19723	0.8	19.2	16.0	-17.93	264	5.292	23959.5	2457.4	20.9	2154	1149	
17	269	521.2	18475	0.0	13.8	15.4	-14.15	294	5.174	23423.5	2469.6	21.0	2095	1117	
17	299	511.2	18124	0.0	31.0	15.0	-12.45	314	6.449	29196.7	2773.7	23.5	2325	1240	
17	319	441.5	15653	0.2	31.0	14.0	-12.01	344	10.903	49361.1	3030.4	25.7	3598	1919	
17	347						nd	364	10.900	49351.0	3030.4	25.7	3597	1918	
17	369	354.8	12579	1.8	16.1	9.9	-4.31								
17		83.8	2972	0.5											

Appendix 2: Photographs and description of organisms retrieved with Agassiz sediment trawls (AGT).

AGT -1

Observations: Small cnidarians (Anthozoa) and polychaete tubes (Maldanidae) dominated the sample. In addition, asteroids, bivalves (*Nucula*), gastropods (*Calliostoma, Aforia, Miomelon* and *Natica*), scaphopods, maldanids polychaetes as well as fishes (*Caelorinchus fasciatus*) were observed. Taxa richness was very low.



Observations: Many stones, probably carbonate and mud breccia were collected. Taxa richness of the fauna was relatively high, consisting of large gastropods (*Calliostoma*, *Aforia*, *Miomelon* and *Zetela*). On these stones a rich epibenthic community had developed with hydrozoans, bryozoans, polychaetes (Eunicidae and Lumbrineridae), and polyplacophorans (*Leptochiton americanus*) and many brachiopods. In addition, bivalves (*Limopsis*, *Cuspidaria* and *Nucula*), ophiuroids (2 species), dendrobranchiata shrimps (*Haliporoides diomedea*), caridean shrimps (*Campylonotus semistriatus*, *Oplophorus novazealandae*), asteroids, cnidarians (sea anemones), ophiuroids (*Astrotoma*) with arms coiled around gorgonians, echinoid, corals (scleractinia), echiurans, ascideas and fishes (*Coryphaenoides ariommus*) were observed.



Note: Chitons (*Leptochiton americanus*) were kept for enzymatic activity analysis (i.e. anaerobic and aerobic metabolism).

Observations: The AGT catch was composed mainly by small bivalves (*Nucula*), gastropods (*Aeneator fontainei*), asteroids (3 species), caridean shrimps (22 *Haliporoides diomedea* and 3 *Stereomastis* sp.), many fishes (20 *Coryphaenoides fasciatus*, 1 *Physiculus luminosus* and 3 Micthophydae) and sharks (2 *Centroscyllum nigrum*, 1 *Halaelurus canescens*). On the other hand, small macrofauna such as gastropods (*Natica*), scaphopoda, polychaetes (Sternaspidae), sipunculids, and reptant crabs (Majidae) were also observed.



Observations: The content of the AGT, after washing the silts, was dominated by many polychaete tubes of Maldanidae (empyt) and scaphopods. Asteroids (2 species), ophiuroid (1 species), large gastropod (*Aeneator*), caridean shrimps (28 *Haliporoides diomedea*), many fishes (16 *Caelorinchus fasciatus*, 2 *Centroscyllum nigrum* and 1 *Halaelurus canescens*), small gastropods (*Homalopoma panamense*, *Zetela* sp), and polychaetes (*Eunice magellanica*).



Observations: Tubes (with animals) of the polychaete *Hyalinoecia chilensis* dominated the sample, carbonatic rocks and stones with a very rich epifauna (sea anemones, briozoans and hydrozoans) were also collected. Large gastropods (*Bathybembyx macdonaldi*, *Aforia goniodes*, and *Callisotoma* sp), polychaetes (*Eunice magellanica*), dendrobranchiata and caridean shrimps (*Haliporoides diomedea*, *Acantephyra pelagica*, *Campylonotus semistriatus* and *Paracrangon sp.*), ophiuroids (2 species), asteroids (1 species), ophiuroids (*Astrotoma*) with arms coiled around gorgonians, large echinoids, corals (Scleractinia), ascideas and fishes (*Caelorinchus fasciatus* and three unknow species) were observed. In addition, fauna inside stones was found (Mollusca: *Leptochiton americanus*, *Natica* sp; Polychaeta: *Eunice* sp, Lumbrineridae and Serpulidae).



Note: Chitons (*L. americanus*) and gastropods (*Aforia goniodes* and *Bathybembyx macdonaldi*) were selected for analysis of enzimatic activity (i.e. anaerobic and aerobic metabolism).

Observations: As in the previous trawl, most of the catch was composed by tubes of the polychaetes Hyalinoecia chilensis and carbonatic rocks and stones. Living chemosynthetic endosymbiont-containing bivalves, Calyptogena gallardoi sp. nov. and Thyasira sp. were collected. In addition valves of Lucinoma sp., and large specimens of a member of the family Vesicomyidae (Archivesica) were also retrieved. Many species of sea anemones, probably associated to cold seeps communities were also found. On the other hand, a high diversity of non-chemosynthetic fauna was also found. An echinoid similar to *Phormosoma*, ophiuroids (Ophiomusium lymani and 2 species), asteroids (3 species), holothuroids (1 species) and sipunculids (1 species), many species of gastropods (Homalopoma panamense, Bathybembyx macdonaldi, Calliostoma sp and Aforia sp), bivalves (Nucula), polyplacophorans (Leptochiton americanus), cephalopods (2 species), scaphopods, caridean shrimps, reptant decapods were also observed (Haliporoides diomedea, Campylonothus semistriatus, pandalidae, and Stereomastis sp). In terms of polychaetes, many individuals of family eunicidae (Eunice sp) and Lumbrineridae were found. On rocks, many species of hydrozoans and briozoans were also observed. Few species of fishes were retrieved (Coryphaenoides ariommus, Centroscyllum nigrum and Raja sp).



Note: This is the first time that living cold-seep fauna is collected in a research cruise along the Chilean margin. Gastropods (*Homalopoma panamense*), bivalves (*C. gallardoi* sp. nov.) and a polychaete (*Eunice* sp.) were selected to analysis of enzimatic activity (i.e. anaerobic and aerobic metabolism).

Observations: Polychaete tubes, *Hyalinoecia chilensis* and carbonatic rocks and stones characterized the sample. Few individuals of the bivalves Calyptogena gallardoi sp. nov., Thyasira sp, and shell fragments of Lucinoma and Archivesica, were also collected. A living bivalve from the Family Solemyidae (Acharax sp) was also found. Two or three tube-like structures, probably of a Siboglinid polychaetes (previously known as pogonophorans) were also found. An important non-chemosynthetic fauna was observed, with an echinoid similar to Phormosoma, the ophiuroids (Ophiomusium lymani and 1 species), asteroids (3 species) and holothuroids (1 species), sipunculids (1 species), many species of gastropods (Homalopoma panamense, Bathybembyx macdonaldi, Calliostoma and Aforia), bivalves (Nucula), polyplacophorans (Leptochiton americanus), cephalopods (1 species), scaphopods, dendrobranchiata, caridean shrimps and reptant decapods were also observed (Haliporoides diomedea, Campylonothus semistriatus, pandalidae, and Stereomastis sp). In terms of polychaetes, many individuals of family eunicidae (Eunice sp) and lumbrineridae and an endosymbiont polychaetes associate to Calyptogena gallardoi sp. nov. were found. Many species of fishes (Coryphaenoides ariommus, Caelorinchus fasciatus, Caelorinchus chilensis, Bothrocara alalongum, Centroscyllum nigrum, Notocanthidae and Alepocephalidae) were also observed.



Observations: Tube-forming polychaetes *Hyalinoecia chilensis* again dominated the sample, but in this catch a very high diversity of individuals from several taxa was observed. Echinoderms and ophiuroids (*Astrotoma* sp.) with arms coiled around gorgonians, crinoids, ophiuroids (*Ophiomusium lymani*, 3 species), asteroids (*Hymenaster* sp., 3 species), holothuroids (1 species), sipunculids (1 species), an echinoids similar to *Phormosoma*, polychaetes Aphroditids (*Aphrodite longirostris*), deep-sea caridean shrimps and reptant decapods (*Campylonotus semistriatus*, *Sclerocrangon atrox*, *Paracrangon* sp., *Munidopsis trifida*, *Munidopsis* sp and *Stereomastis* sp), many species of gastropods (*Homalopoma panamense*, *Bathybembyx macdonaldi*, *Calliostoma* and *Aforia*) and scaphopods were observed. Many species of fishes (*Coryphaenoides ariommus*, *Caelorinchus chilensis*, *Bothrocara alalongum*, *Centroscyllum nigrum*, Notocanthidae and one unknow species) were also observed. In terms of small fauna, some individuals of the isopods similars to *Cirolana* and *Aega* were found. In spite of the vicinity with two previous trawls, no methane seep related fauna was observed.



Observations: The content of the AGT was composed by many individuals of the polychaete *Hyalinoecia chilensis*. One individual of the large vesicomyids (*Archivesica* sp.) was retrieved alive, as well as many individuals of the smaller *Calyptogena gallardoi* sp. nov. In addition, a large tube (about 1m) with black patches evidencing that it has been buried in sulphidic sediment and probably belonging to a Siboglinid polychate was also found. On the other hand, an rich non-chemosynthetic community was observed. Ophiuroids (*Ophiomusium lymani* and 2 species), ophiuroids (*Astrotoma* sp.) with arms coiled around gorgonians, asteroids (3 species), holothuroids (1 species), fishes (*Halaelurus canescens, Caelorinchus chilensis, Centrosyllun nigrum*, Notocanthidae and Alepocephalidae), dendrobranchiata, caridean shrimps and reptant decapodos (*Haliporoides diomedea, Acantephyra pelagica, Sclerocrangon atrox, Campylonotus semistriatus*, Pandalidae, *Munidopsis trifida* and *Munidopsis* sp), polychaetes (*Eunice magellanica* and *Eunice* sp.) and an endosymbiont polychaete associate to *Calyptogena gallardoi* sp. nov., scaphopods and gastropods (*Homalopoma panamense* and *Bathybembyx macdonaldi*) and the polyplacophoran (*Leptochiton americanus*) were observed.



Note: Foot and gill tissue from the large vesicomyid was saved for enzimatic activity (i.e. anaerobic and aerobic metabolism).

Observations: The content of the AGT was composed by many rocks, gorgonarians and ophiuroid (*Astrotoma* sp., 1 species) with arms coiled around gorgonians. On these stones a nice epibenthic community had developed with hydrozoans, bryozoans, polychaetes (*Eunice* sp., Sabellidae and Lumbrineridae) and polyplacophorans (*Leptochiton americanus*), brachiopods, sipunculids (1 species), holothuroids (2 species), asteroids (*Hymenaster* sp. and 2 species), ophiuroids (*Ophiumusium lymani*, 3 species), fishes (*Halaelurus canescens, Centroscyllum nigrum* and *Caelorinchus fasciatus*), dendrobanchiata, caridean shrimps and reptant decapods (*Haliporoides diomedea, Campylonotus semistriatus, Munidopsis trifida, Munida curvipes, Munidopsis* sp. and *Trachycarcinus hystricosus*), gastropods (*Bathybembyx macdonaldi, Fusitriton magallanicus, Calliostoma chilena* and *Trophon*) were observed. In addition, rest of bivalves associated to cold seep communities were also found (Vesicomyids, *Acharax, Lucinoma* and *Thyasira*).





AGT -11 Observations: This sample, taken off Lebu, was composed of many forams (*Rhabdammina*), asteroids (3 species), echinoderms similar to *Phormosoma* and *Echinus*, ophiuroids (2 species), fishes (*Coryphaenoides ariommus* and Notocanthidae), caridean shrimps (*Stereomastis* sp. and Oplopharidae), bivalves (*Nucula*), gastropods (*Miomelon*), polychahetes (Ophelidae) and sea pens (Tunicates). A carbonate block about 2 kg with evidences of being exposed to sulphide was also retrieved.







AGT -12

The gear apparently did not touch the bottom and no fauna was retrieved.

Observations: In this AGT, most of the catch was composed by tubes of the polychaetes *Hyalinoecia chilensis* as well as carbonatic rocks and stones. Three living chemosynthetic endosymbiont-containing bivalves, *Calyptogena gallardoi* sp. nov. and *Thyasira* sp. were collected. Many species of sea anemones, an echinoid similar to *Phormosoma*, ophiuroids (*Ophiomusium lymani* and 2 species), asteroids (3 species), holothuroids (1 species), many species of gastropods (*Bathybembyx macdonaldi*, *Calliostoma* sp. and *Aforia* sp), cephalopods (1 species), caridean shrimps, reptant decapods were also observed (*Haliporoides diomedea*, *Campylonothus semistriatus*, *Munidopsis trifida*). In terms of polychaetes, many individuals of family Eunicidae (*Eunice* sp.) and Lumbrineridae were found. On rocks, many species of hydrozoans, briozoans and brachiopods were also observed. Few species of fishes were retrieved (*Coryphaenoides ariommus*).



Note: Foot and gill tissue from *Calyptogena gallardoi* sp. nov. was saved for enzimatic activity (i.e. anaerobic and aerobic metabolism).